Nano Research 2018, 11(6): 3065–3087
https://doi.org/10.1007/s12274-018-2068-y
Review Article
ISSN 1998-0124
CN 11-5974/O4

Recent progress on printable power supply devices and systems with nanomaterials

Yuanjing Lin[1], Yuan Gao[1,†], Fang Fang[2] (✉), and Zhiyong Fan[1] (✉)

[1] *Department of Electronic and Computer Engineering, The Hong Kong University of Science and Technology, Hong Kong, China*
[2] *Department of Materials Science, Fudan University, Shanghai 200433, China*
[†] *Present address: Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong, China*

Received: 2 February 2018
Revised: 14 March 2018
Accepted: 2 April 2018

KEYWORDS

printing techniques, energy conversion, energy storage, integrated self-powered system

ABSTRACT

In recent years, tremendous research interest has been triggered in the fields of flexible, wearable and miniaturized power supply devices and self-powered energy sources, in which energy harvesting/conversion devices are integrated with energy storage devices into an infinitely self-powered energy system. As opposed to conventional fabrication methods, printing techniques hold promising potency for fabrication of power supply devices with practical scalability and versatility, especially for applications in wearable and portable electronics. To further enhance the performance of the as-fabricated devices, the utilization of nanomaterials is one of the promising strategies, owing to their unique properties. In this review, an overview on the progress of printable strategies to revolutionize the fabrication of power supply devices and integrated system with attractive form factors is provided. The advantages and limitations of the commonly adopted printing techniques for power supply device fabrication are first summarized. Thereafter, the research progress on novel developed printable energy harvesting and conversion devices, including solar cells, nanogenerators and biofuel cells, and the research advances on printable energy storage devices, namely, supercapacitors and rechargeable batteries, are presented, respectively. Although exciting advances on printable material modification, innovative fabrication methods and device performance improvement have been witnessed, there are still several challenges to be addressed to realize fully printable fabrication of integrated self-powered energy sources.

1 Introduction

Wearable and portable electronics, for their attractive form factors such as lightweight, excellent flexibility, remarkable operation safety and supreme compatibility with human bodies, have become widely practical in the fields of wireless communications, multifunctional entertainments, personal healthcare and monitoring,

Address correspondence to Zhiyong Fan, eezfan@ust.hk; Fang Fang, f_fang@fudan.edu.cn

etc. [1–4]. In most cases, these electronics are driven by power sources. Energy storage devices, such as batteries and supercapacitors, are most commonly adopted in commercial wearable and portable electronics. However, such energy storage devices require external power sources for charging. In recent years, the concept of a "self-powered system" has been introduced, which generally refers to systems whose energy can be directly harvested from solar radiation, body movement bioenergy and so on, and further converted to electricity to power up functional electronic devices [5–7]. Generally, the energy harvesting and conversion are realized by solar cells [8, 9], nanogenerators (e.g., piezoelectric and triboelectric generators) [5, 10], electrochemical fuel cells (e.g., biofuel cells (BFCs)) [11, 12], etc. To realize continuous functionality without energy interruption from surrounding condition variation factors, it is highly desirable to integrate functional electronic devices and energy harvesting/conversion devices with energy storage devices into infinitely self-powered energy sources [13, 14].

In the past decades, the fabrication of energy conversion and storage devices has been primarily relying on conventional techniques, due to their mature fabrication procedures. For instance, photolithography was frequently adopted for patterning [15, 16], and chemical vapor deposition [17, 18], sputtering [19], and atomic layer deposition [20] methods were well developed for active material preparation. However, these techniques usually not only involve complicated multistage procedures but also require harsh operation conditions, either dust-free or high vacuum, which raises the fabrication cost and limits the scalability of the products [21]. While conventional solution processes, such as spin coating, are relatively facile approaches for thin film deposition, the relatively low scalability and flexibility for patterning make them less attractive for next generation energy devices [22]. In comparison, printing techniques, such as well-developed screen printing and inkjet printing, and the emerging novel three-dimensional (3D) printing and laser writing, provide scalable, cost-effective and facile approaches for fabrication of flexible, wearable and miniaturized power supply devices, which have drawn tremendous research interest these years [6, 23]. Furthermore, extensive studies were performed on the synthesis and modification of nanomaterials for printing techniques, and exciting advances were seen in printable device fabrication and performance improvement, etc. [24–27]. Notably, both energy conversion devices and energy storage devices have been successfully fabricated by printing techniques, and even integrated systems have been realized by a printable approach [26], which further demonstrates the feasibility of printable fabrication of power supply devices and their integration into systems.

In this review, we first summarize different printing techniques for power supply device fabrication, highlighting their advantages and limitations. Thereafter, the research progress on novel printable energy harvesting and conversion devices, including solar cells, nanogenerators and BFCs, and the research advances on printable energy storage devices, namely, supercapacitors and rechargeable batteries, are presented, respectively. Meanwhile, several printable strategies aimed at device performance enhancements are also discussed. Afterwards, printable integrated self-powered energy sources, which are still in the infancy stage of development, are introduced [6]. This review provides an overview on the progress of printable strategies combined with the merits of nanomaterials, so as to revolutionize the fabrication of power supply devices and integrated systems with attractive form factors for application in the next generation of portable and flexible electronics.

2 Brief overview of printing techniques for device fabrication

Printing techniques have been widely employed in portable and wearable electronic device fabrication, such as transistors [28–31], photodetectors [32, 33] and sensors [34–38], etc. Compared with conventional fabrication techniques that impose rigid requirements on the materials and substrates, printing methods, e.g., screen printing, inkjet printing, 3D printing and laser writing, enable large scale fabrication on a variety of substrates, thereby providing desirable versatility. For example, by utilizing 3D printing, customized design of health care device modules that fit the needs of individual users can be realized in a facile manner [34]. Among the properties of different techniques, the most critical factors, including patterning resolutions,

pattern design versatility, printing speed, printable material properties and utilization rate, are listed in Table 1 for better comparison.

Screen printing is a mass production method, which can be simply realized by pressing the liquid-phase materials to penetrate through the patterned mask/stencil with a squeegee [39]. Notably, its resolution is mainly limited by mask fabrication techniques, and the patterning quality highly depends on ink formulations and their affinity to substrates. It is reported that the printing quality can be significantly influenced by the strength of mesh materials (e.g., stainless steel, polyester) for printing masks. Besides, appropriate ink viscosity that allow desirable diffusion through the mask without dispensing out the patterned area enables high patterning resolution and fine edges. Studies on wettability of the printable inks to substrates are also critical to improved printing quality [40]. It is reported that a resolution of 6 μm can be achieved with a well-defined stencil and ink with tuned viscosity (Fig. 1(a)) [41], which is much superior to most of the reported data in a range

Table 1 Summary and comparisons of form factors for (a) screen printing (reproduced with permission from Ref. [39], © Springer Nature 2016), (b) inkjet printing (reproduced with permission from Ref. [45], © Elsevier 2009), (c) 3D printing (reproduced with permission from Ref. [52], © Wiley-VCH 2013), and (d) laser-based printable strategies (reproduced with permission from Ref. [58], © National Academy of Sciences 2015)

	Screen printing	Inkjet printing	3D printing	Laser-based
	(a) Squeegee, Ink, Screen mask	(b)	(c)	(d)
Resolution	> 6 μm	> 2 μm	> 10 μm	> 500 nm
Material requirement	High viscosity Shear thinning behavior	Low viscosity	Shear thinning behavior Quick solidification	Thermally convertible
Material utilization	Certain wastage	DOD	DOS	*In situ* patterning
Design versatility	Maks defined	Maskless	Maskless	Maskless
Speed	c.a.70 m·min^{-1}	c.a.1 m·min^{-1}	< 4 m·min^{-1}	< 10 cm·min^{-1}

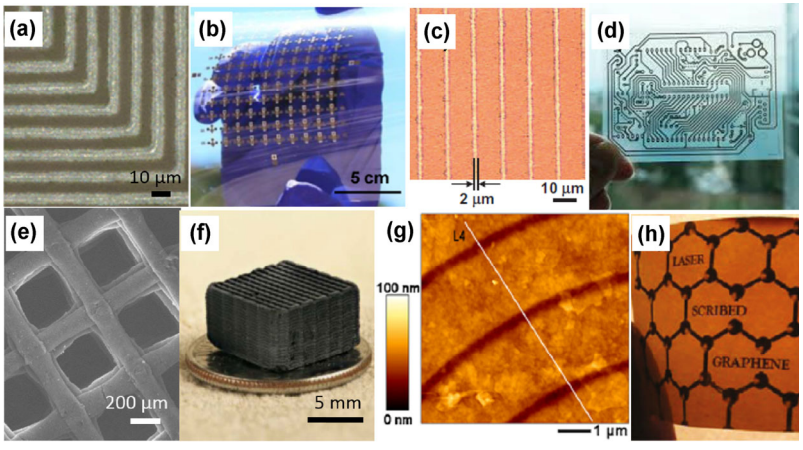

Figure 1 The highest resolutions and prototypes of different printing techniques. (a) Screen printed Ag with a resolution of 6 μm (reproduced with permission from Ref. [41], © Kuroda Electric Czech s.r.o. 2018). (b) Large scale screen-printed pattern arrays on a flexible PET substrate (reproduced with permission from Ref. [21], © American Chemical Society 2014). (c) Inkjet-printed Ag lines with a width of 2 μm (reproduced with permission from Ref. [30], © National Academy of Sciences 2008). (d) Programmable inkjet printed circuit on PET (reproduced with permission from Ref. [46], © ACM International Conference on Ubiquitous Computing 2013). (e) SEM images of a 3D-printed graphene aerogel microlattice with resolution in the microscale and (f) 3D-printed graphene aerogel microlattice with large thickness (reproduced with permission from Ref. [54], © Nature Publishing Group 2015). (g) rGO pattern with a resolution of 500 nm realized by femtosecond laser reduction (reproduced with permission from Ref. [55], © Elsevier 2010). (h) Programmable LSG patterns on PET (reproduced with permission from Ref. [56], © American Chemical Society 2012).

of tens to hundreds of micrometers [39]. Although screen printing has relatively low design flexibility, it is still one of the most widely used printing techniques. Especially for large-scale and mass fabrication, its high printing speed of around 70 $m \cdot min^{-1}$ is much better than most of the other printing methods [6, 23]. Apart from the high throughput for scalable fabrications of pattern arrays, screen printing allows a wide range of printing materials that contain large aspect ratio fillers or high concentrations and can be applied on both rigid (e.g., silicon wafer, glass) and flexible substrates (e.g., textiles, poly(ethylene terephthalate) (PET), as shown in Fig. 1(b)) [21, 42]. These appealing features have made screen printing widely practical for electronic device fabrication.

Compared with screen printing, inkjet printing (IJP) is a drop-on-demand (DOD) material deposition method with superior printing resolution and uniformity. Driven by thermal or piezoelectric excitation, ink droplets are ejected through micro-nozzles (in the range of tens of micrometers) onto substrates [22]. Under appropriate conditions, such as enough printing dots per inch (DPI), these individual droplets could spread and gather together to form a continuous line or film in programmable patterns with controllable thickness by controlling cycle numbers of printing passes [43]. Research efforts have been emphasized on modification of solvent systems for printable inks, considering viscosity, composition and concentration, which play a significant impact role in the smooth printing of high-quality patterns. Generally, the viscosity of inks should be tuned in the range of 5 to 20 cP, and specific surfactants are usually adopted to ensure good dispersion of the nanoparticles inside the printing inks without agglomeration, so as to avoid nozzle clogging [27]. Besides, developing methods for effective interface engineering are critical prerequisites to achieve high resolution and well-defined printing patterns [24, 28, 44, 45], for instance, plasma treatment, preheating of both substrates and printing materials to achieve proper wettability of the substrate, as well as fine control over ejected ink amount. High resolution can also be realized with inkjet printing equipment optimization. For instance, printed conductive and uniform Ag with a line width of 2 μm (Fig. 1(c)) has been achieved with a sub-femtoliter inkjet printing system developed by Sekitani and co-workers [30]. Although several kinds of colloidal inks have been well-formulated and functional electronic circuits have been successfully printed on flexible substrates via a one-step inkjet printing method (Fig. 1(d)) [46–48], aspect ratios of active material fillers are highly restricted by nozzle size [49]. Besides, to obtain a useful device, it is necessary to print each layer of the electronic circuit with certain thicknesses, typically several hundreds of nanometers. In this case, it requires multiple printing passes, which decreases the fabrication efficiency.

To address the above issue, the novel 3D printing techniques that enable programmable layer by layer additive manufacturing open up the possibility of the design of complicated device geometries from the nanoscale to macroscale in a printable manner, and provide a facile approach to fabricating 3D structures with accurate control over device geometry, including dimensions and porosity [26, 27, 50]. In this review, 3D printing techniques refer to the extrusion deposition of colloidal gel, which employs a three-axis motion stage to create patterns by robotically squeezing material through a micro-nozzle [26]. In such a process, shear-thinning behavior and quick solidification of the inks are critical factors to ensure the printing quality [27, 51, 52], especially for shear thinning behavior, which refers to the viscosity decrease under shear strain, as such a physical property change could control the fluidity of the inks. To tailor the ink rheology, electrically insulating additives, such as viscosifiers and ultraviolet light (UV) curable gels, are normally adopted. However, these additives would decrease the ink conductivity and limit the printing resolution. Up to now, the record for 3D printing resolution has been achieved with polylactic acid (PLA) patterns with a minimized line width of 10 μm realized by a novel method combining electrohydrodynamics and fused deposition modeling (E-FDM) [53], and such a value is still inferior to those obtained by inkjet printing and screen printing methods. Therefore, the as-built 3D architectures are normally in a macro scale, as shown in Figs. 1(e) and 1(f) [54]. As the reported ink formulations for 3D printing of electronics are still limited and require further optimization, thorough study on the desirable material

properties for such printing fabrication methods is of significance, so as to enable enhancement of printing resolution and the performance of as-printed devices [27].

Differing from the printing techniques discussed above in which the printable materials are usually prepared by dispersing active materials in a solvent to form inks, laser writing relies on melting, sintering or chemical conversion of functional materials into a designed geometry with the thermal energy delivered by the laser [26]. The laser beam goes along the programmed path on the pre-deposited materials and realizes a precise pattern with a reported highest resolution of up to 500 nm (Fig. 1(g)) [55]. Particularly, graphene oxide (GO) is the most widely utilized thermally convertible material, as it can be *in situ* converted to porous reduced graphene oxide (rGO) on a variety of flexible substrates (Fig. 1(h)) [56–58]. Moreover, the electrical properties of such laser-scribed graphene (LSG) can be precisely tuned with laser intensity and irradiation treatments. In addition to GO, a variety of two-dimensional (2D) materials, such as molybdenum disulfide (MoS_2), molybdenum trioxide (MoO_3), tungsten disulfide (WS_2) and boron nitride (BN) nanosheets, have been prepared into stable suspensions for demonstration of printable electronics [59]. For instance, 2D MoS_2 films were patterned into micro electrodes by laser writing and served as electrochemical active materials for pseudocapacitors, which was attributed to oxidation states of Mo atoms from +2 to +6 and the easy ion access into multi-layered structures [60]. However, materials for laser-based printing techniques are not yet fully explored, especially for energy devices. Besides, such processes require a low laser scanning speed to generate continuous heat for localized physical/chemical reactions of the patterned materials and thus reduce the fabrication efficiency, as shown in Table 1. Therefore, it requires collaborative efforts from both academia and industry to tackle these technical issues [26].

In addition to the printing techniques discussed above, a variety of printable strategies including gravure printing, transfer printing and aerosol jet printing (AJP), also attract research interests and have been utilized in successful demonstrations of printable functional devices [40]. Gravure printing is a contact printing technique that transfers materials through capillary action from a gravure cylinder to substrate in a roll-to-roll manner. Its capability for mass production makes it one of the widely utilized methods for printable electronics [40]. Cho's group demonstrated the possibility to produce a 13.56 MHz 1-bit radio frequency identification (RFID) tag in a low-cost fully gravure-printed process [61]. Such devices convert a low-power radio frequency (RF) signal into a higher power output and can also be printed onto paper, which is desirable for flexible and portable electronic devices [62]. One of the challenges for gravure printing is to achieve uniform patterns with fine edges, which could be optimized with soft blanket gravures [63]. Besides, the printing resolution (ca. 50–200 μm) and pattern designs are largely limited by the patterns on gravure cylinders, which are produced by mainly relying on laser cutting or electromechanical approaches, and the replacement of such cylinders increases the maintenance cost [40]. Another well-developed contact printing method is transfer printing, which enables high throughput mechanical assembly of material/device arrays. Such a printing method relies on the switching of adhesion properties of polymeric stamps between different substrates [40]. With the assistance of transfer printing, Roger's group developed a scalable approach for stacking microscale solar cells into quadruple-junction four-terminal modules (active area of 600 μm × 600 μm) with a remarkably high power conversion efficiency (PCE) up to 43.9% [64]. In recent years, AJP as a mask-free non-contact DOD printing method has attracted increasing research interest. Differing from direct ejection of ink droplets in IJP, an aerosol is generated by atomization or ultrasonication of liquid inks and is subsequently focused with sheath gas streams in the deposition nozzles. The as-printed pattern quality can be precisely tuned with atomizer flow rate and sheath flow rate. In such a process, nozzle clogging can be avoided and as-deposited line widths can be minimized to sub 10 μm, which is far less than the nozzle diameters [65]. Besides, variation on the nozzle-to-substrate distance in the millimeter range introduces negligible change in the as-printed patterns as a result of the focused aerosol stream, thus providing desirable

compatibility on 3D structured surfaces [66]. There are several reports on the application of AJP in thin film deposition, especially for metal contact preparation in the solar cell field. However, it is still a less-established printable strategy and requires more research efforts to tackle the challenges, including ink formulation to produce stable monodisperse aerosols with an atomization process, low temperature post-treatment to be compatible with flexible substrates and eliminating sprinkle spots to produce fine-edged patterns [65, 66]. Recently, Durstock's group developed reproducible fabrication of highly uniform and defect-free perovskite films in ambient environment and achieved a PCE of up to 15.4% (active device area of 0.1 cm^2) [67]. Such a process is less labor intensive and demonstrates advantages over the conventional solution approach for perovskite fabrication.

Because of their unique features such as remarkable scalability and flexibility of the fabrication process, and considerable control over the as-printed architectures, printing techniques have been utilized for the fabrication of a variety of devices, especially for power devices that have relatively high tolerance of fabrication conditions and device architecture designs. Generally, printing techniques are utilized to prepare part of the devices, and fully printable devices are still rarely reported, mainly due to the challenges in synthesizing printable materials for the whole device fabrication and solvent spreading between different printed layers [6, 24, 27]. To tackle these issues, extensive research efforts have been focused on device architecture revolution and material engineering toward fully printable fabrication procedures, and the research advances will be introduced in the following sections.

3 Printable energy conversion devices

Energy from the surroundings such as sunlight, wind and even the human body can be harvested and converted to electricity by solar cells, nanogenerators, BFCs, etc. Printing techniques provide novel fabrication routes to build such energy generators onto a variety of flexible and light weight substrates, which are preferable for wearable self-powered electronics. In this section, we focus on the research progress concerning printable energy conversion devices.

3.1 Solar cells

Renewable and clean solar energy can be converted into electrical energy by a solar cell based on the photovoltaic effect, which is considered as one of the most effective approaches to utilizing sustainable energy and a preferred and optimal solution to reduce dependence on traditional energy resources [23]. In general, when the absorbed incident photon energy is greater than the band gap of the semiconductor materials in the solar cell, electron–hole pairs will be generated. These charge carriers are then separated by the existing electric field in the cell and extracted to an external circuit to form electrical current. The well-known solar cells include silicon-based solar cells, organic solar cells (OSCs), dye-sensitized solar cells (DSSCs) and perovskite solar cells (PVSCs); because of their own attributes and advantages, they have attracted tremendous research interest in recent years. Conventionally, the fabrication of solar cells relies on vacuum deposition techniques (e.g., thermal evaporation, sputtering) and solution processes (e.g., spin coating), in which the active materials are deposited or spin coated layer by layer. However, device area is normally limited by the chamber size of the equipment and thus reduces the scalability of the device fabrication. In comparison, printing techniques provide effective routes to produce large-scale and flexible solar cells for practical applications. Research on printable solar cells mainly focuses on revolutions in device structures that can be adapted to facile printing procedures. Meanwhile, optimization of the printed material quality was investigated so as to realize solar cells with desirable device area, competitive PCE, and considerable stability, which are critical parameters for device performance evaluation [68].

Ever since the first thin film solar cell was fabricated by screen printing of the active layer in 2001 [69], research interests have been raised in synthesizing printable photovoltaic materials and seeking optimal device structures to realize low cost, facile and scalable fabrication of solar cells without compromising device performance. At the early stage, a variety of nanocrystal inks were successfully synthesized, demonstrating

the feasible concept of printable photovoltaics [70–72]. For instance, in 2008, Panthani and co-workers synthesized copper indium gallium selenide (CIGS) nanocrystal inks and further produced working devices by a printing technique [71]. However, the research progress in fully printed solar cells was hindered by several challenges, such as the lack of high quality solution-processable materials and complexity of multilayer device structures that required dedicated interface engineering. In 2015, Brabec's group demonstrated fully printed tandem OSCs with printed Ag and Ag nanowire network as the electrode combined with proper interface engineering (Fig. 2(a)). The as-fabricated devices with active area of 10.4 mm^2 achieved enhanced PCEs on both rigid (5.81%) and flexible substrates (4.85%), compared with previous reported printable OSCs [73].

The printable fabrication strategy can be also applied in fabrication of a variety of solar cells. In 2015, Lund's group reported the fabrication of a DSSC by inkjet printing an ionic liquid electrolyte, and thus eliminating the complicated steps of hole drilling and sealing, which are normally required in conventional processes. The as-fabricated printed electrolyte based solar cells delivered promising performance with a 100% retention after over 1,100 hours aging [74]. In another work from the same group, a highly controllable and fast dye-sensitized process by inkjet printing was developed, as shown in Fig. 2(b) [75]. Compared with conventional time-consuming fabrication processes for dye molecule absorption onto photoelectrode films, such a fast and cost-effective fabrication process allowed precise control over dye loading to create DSSCs with tailored transparency and versatile patterns. More significantly, the obtained performance and stability by inkjet printing were the same as the devices that were fabricated with a conventional drop casting process. These research contributions showed a promising route toward fully printable DSSC.

In recent years, organic-inorganic metal halide perovskite solar cells have attracted tremendous research interests due to their appealing properties, such as tunable bandgap, high carrier mobility, solution-process compatibility and high energy conversion efficiencies over 22% [14, 76]. However, it is still a challenge to fabricate perovskite solar cells via printing methods because of the high material sensitivity to humidity and easy decomposition under

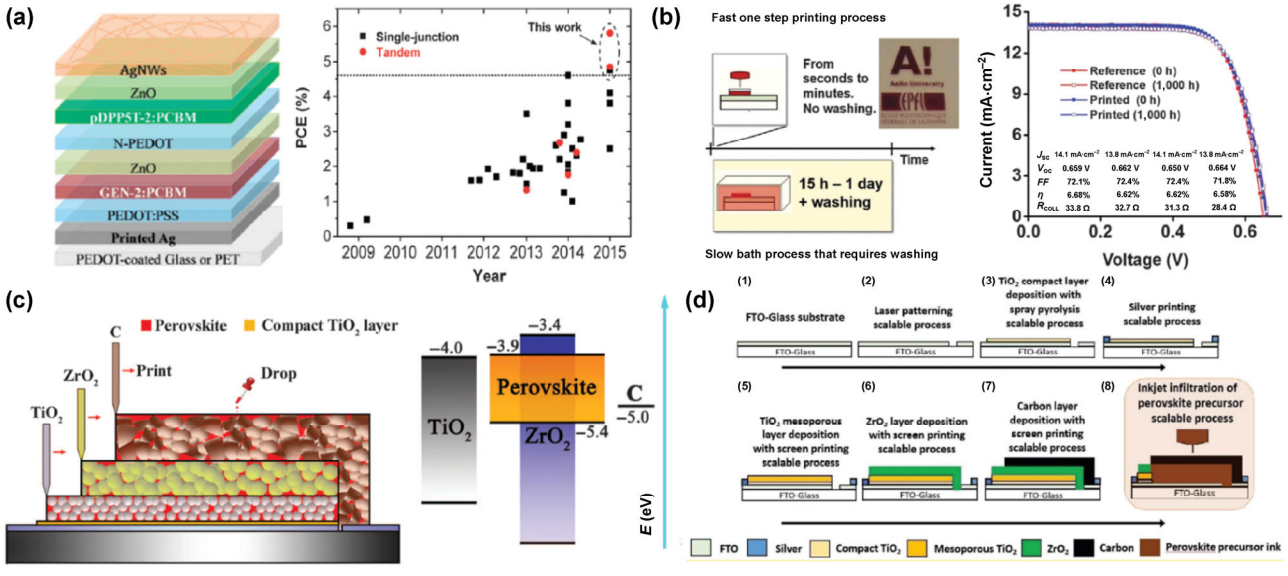

Figure 2 Research progress on printable solar cells. (a) Schematic illustration of the device structure of fully printed organic tandem solar cells and efficiency evolution of fully printed organic solar cells (reproduced with permission from Ref. [73], © Royal Society of Chemistry 2015). (b) Inkjet printing electrolyte for facile fabrication of DSSC with pattern design versatility and equal performance to conventionally prepared devices (reproduced with permission from Ref. [75], © Royal Society of Chemistry 2016). (c) Schematic diagram of fabrication process of HTL free, fully printable perovskite solar cells and the corresponding band diagram (reproduced with permission from Ref. [78], © American Association for the Advancement of Science 2014). (d) Schematic diagrams of the air processed fabrication procedures of printable and scalable perovskite solar cells (reproduced with permission from Ref. [76], © Wiley-VCH 2017).

ambient conditions [77]. Normally, a perovskite solar cell consists of hole transporting layer (HTL), electron transporting layer (ETL), perovskite layer and two electrodes. Based on a novel device structure without an HTL [78, 79], Han's group successfully demonstrated for the first time a fully printable PVSC with a PCE of 6.64% from an exposed device area of 0.125 cm^2 [80], and continuous research efforts were emphasized on interface engineering and material formulation for performance improvement [81–85]. For instance, as shown in Fig. 2(c), the perovskite solution was infiltrated into a triple-layer scaffold consisting of mesoporous TiO_2, ZrO_2 and porous carbon film, which can be prepared by screen printing. A PCE of 12.8% on a device with an active area of 0.0725 cm^2 was achieved by introducing 5-ammoniumvaleric acid (5-AVA) cations into the perovskite solutions, which resulted in lower defect concentrations in perovskite crystals and better surface contact with TiO_2 [78]. With such novel device architectures and printable strategies, large scale PVSCs with areas up to 100 cm^2 have been demonstrated with considerable PCE and stability [86]. Besides, by combining different solution processes, printable fabrication of scalable PVSC panels was also successfully achieved in ambient condition by Hashmi and co-workers, as shown in Fig. 2(d) [76].

The bottleneck factors hindering further improvement of the PCEs of printable solar cells mainly lie in: 1) The printing fabrication process may fail to form satisfactory interface morphology, thus introducing the risk of device failure due to defects and/or high carrier recombination ratio [81, 87]. Therefore, modification of printable materials and surface morphology is critical for device performance enhancement. For instance, by formulating the solvent system for polymer donor inks, Hoth et al. realized surface roughness control of printed polymer thin films, which contributes to the PCE improvement of as-fabricated OSCs [88]. 2) Thin films prepared by conventional printing procedures generally exhibit poor crystallinity, which results in low carrier mobility. To solve this problem, Minemawari et al. developed a novel dual-nozzle inkjet printing method to produce single crystal films. Specifically, an antisolvent was first printed and then active materials were printed onto the confined area. Such antisolvent crystallization methods produce thin films with uniform crystallization at the liquid–air interface, which can be adopted to fabrication of high efficiency printable solar cells [87].

3.2 Other types of energy conversion devices

It is worth mentioning that solar/light energy can also be converted into mechanical energy based on volume contractions of light-sensitive molecules [89]. Such photomechanical systems demonstrate potential applications in self-powered micro/nanomachines. Apart from solar energy, mechanical energy such as vibration or friction can be easily collected from the environment or human body. However, as the research on printable fabrication of such energy devices with printing methods is still in a less developed stage, the performances are not yet optimized.

Electrical charges can be generated in piezoelectric materials when mechanical stress/strain is applied. Printing techniques such as screen printing and 3D printing have been applied in processing ceramic piezoelectric materials, such as lead zirconate titanate (PZT) and barium titanate (BTO), to realize mass production and create porous structures with enhanced piezoelectric properties [50, 90, 91]. Emamian and co-workers fabricated fully printable piezoelectric devices on various flexible substrates by screen printing, as shown in Fig. 3(a) [92]. Poly(vinylidene fluoride) (PVDF) as the piezoelectric material was screen-printed and sandwiched between printed silver (Ag) electrodes. Such piezoelectric devices functioned as both touch sensors and force sensors to provide output signal proportional to the applied forces and demonstrated promising application in human–machine interfaces. By coupling the piezoelectric and semiconducting properties of zinc oxide (ZnO) nanowires to effectively convert mechanical energy into electric power output, Wang's group first demonstrated the concept of piezoelectric nanogenerators (PENGs) in 2006 [5]. Following this work, triboelectric nanogenerators (TENGs) were demonstrated to generate electricity by utilizing an electrostatic phenomenon when a friction force was applied, which aroused tremendous research interest to explore a variety of materials with large power output [10]. The high compatibility of printing methods enables the fabrication of nanogenerators with attractive form factors. Recently, 3D printable

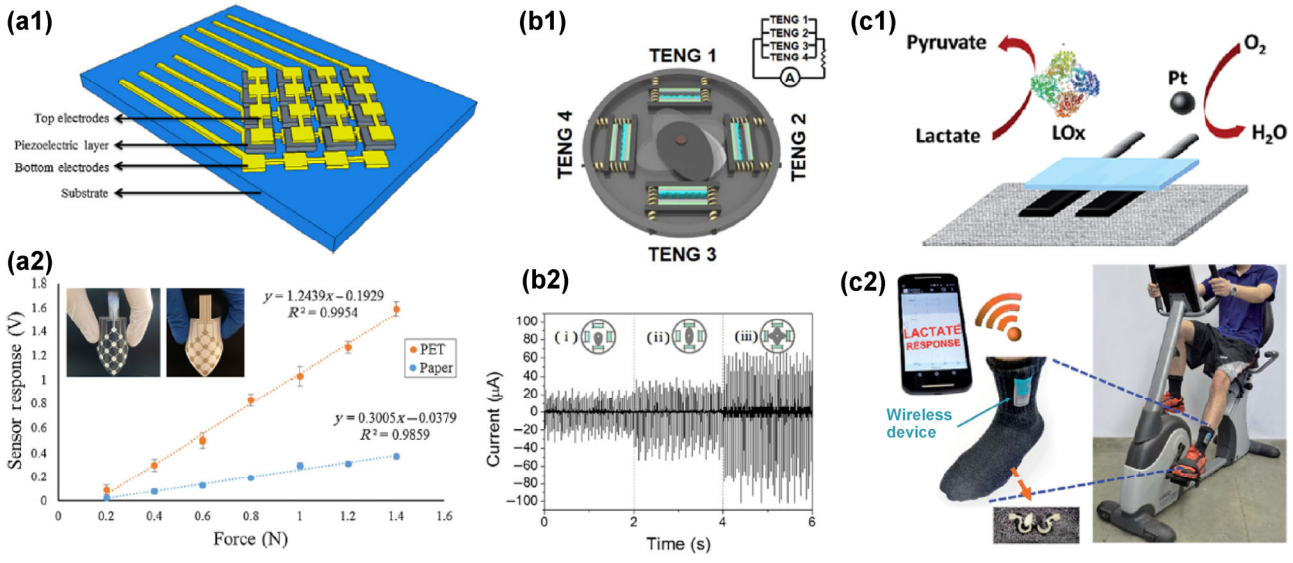

Figure 3 Demonstrations of different kinds of energy conversion prototypes. (a) Fully printed PVDF-based piezoelectric generators fabricated on PET and paper (reproduced with permission from Ref. [92], © Elsevier 2017). (b) Triboelectric generators on 3D printed templates (reproduced with permission from Ref. [93], © Elsevier 2017). (c) Wearable BFCs integrated into a self-powered lactate monitor system (reproduced with permission from Refs. [2, 94], © Copyright Royal Society of Chemistry 2014 and 2016, respectively).

cam-based TENGs were also fabricated by Lee et al. to transform rotational motion into electricity, as shown in Fig. 3(b) [93]. In such a TENG, most of the components are fabricated by 3D printing of PLA, which is a cost-effective and non-toxic strategy by utilizing a considerably durable material. Besides, 3D printing also provides design versatility on cam shapes and integration of single to quad TENG device units, to produce various levels of power output.

Bioenergy harvesting devices such as enzymatic biofuel cells (BFCs) also receive considerable attention due to the non-invasive method to convert energy from biofluids, such as sweat into electricity. The glucose and lactate in the biofluids can be oxidized by enzymatic reaction at the anode and oxygen reduced at the cathode, and thus generate considerable electrical power output [3]. Wang's group reported stress-enduring functional materials to convert bioenergy into electricity [94]. In this work, body-compliant glucose and lactate biofuel cells were successfully fabricated onto textile and highly stretchable fiber by screen printing. As a proof-of-concept, a self-powered system that realizes real time monitoring of lactate and wireless signals transmission was successfully fabricated, as shown in Fig. 3(c), and such BFCs have also been demonstrated in the forms of tattoos, self-powered LED bands and watches [2, 12, 94].

In these energy conversion devices, nanostructures that provide large surface area are capable to harvest more energy and achieve higher energy conversion efficiency. Therefore, future research efforts should be focused on optimization of printable inks and recipes to create complex nanostructures with higher aspect ratios and larger surface areas by printing technologies.

4 Printable fabrication of energy storage devices

Energy storage devices, serving as stand-by power supplies, are indispensable components of self-powered systems. These devices could release energy via reversible physical and/or chemical reactions to maintain the electronic system non-stop working. Typically, supercapacitors and rechargeable batteries are two primary types of electrochemical energy storage devices with essentially different energy storage mechanisms, which will be further illustrated in the following sections. In recent years, a rapid progress in printable fabrication of energy storage devices with attractive attributes, such as high energy storage and power density, stable cycling capability, enhanced

operational safety, remarkable flexibility and miniaturized form factor, has been reported. It is worth mentioning that morphologies with large surface-to-volume ratio can provides adequate sites for charge storage and ion contact, which is critical to realize high performance of energy storage devices. Therefore, certain roughness or porosity is desirable in fabrication for energy storage devices, which makes them more feasible to be fabricated by printable methods, especially compared with printable solar cells that generally requires smooth surfaces. Besides, planar configurations that consist of interdigitated electrodes separated on one plane are preferred in fabrication of printable and miniaturized supercapacitors/batteries [23]. Such planar device configurations also allow rapid electrolyte ion transportation and short ion diffusion distance between electrodes, and thus provide higher power capability [15, 95–98]. In this section, the advantages of printable fabrication of such energy devices will be introduced and strategies toward performance enhancement will be discussed.

4.1 Supercapacitors

Supercapacitors, also known as electrochemical capacitors, are being utilized to bridge the performance gap between traditional capacitors and rechargeable batteries [99]. Generally, supercapacitors possess large electrode surface area and multiple charge storage mechanisms (physical adsorption and chemical reaction) and are capable to store much higher energy than electrostatic capacitors and electrolytic capacitors [100]. In addition, supercapacitors can deliver the energy much faster than rechargeable batteries due to their fast surface electrochemical reactions, thus these devices are commonly utilized in applications such as regenerative brakes in electric vehicles and pacemakers in medical treatment, where batteries have a relatively low power output and the traditional capacitors fail to meet the high energy requirements [99]. Based on different energy storage mechanisms, supercapacitors could be further classified into two categories. Generally, carbon-based materials, such as activated carbon, graphene, and carbon nanotubes, are widely used as electrode materials where energy is stored by physical ion absorption, and such a type of supercapacitor is named as an electrical double layer capacitor (EDLC) [99, 101]. It should be noted that the theoretical capacitances of carbon-based materials are relatively low due to the limited electrolyte ion adsorption at the electrode/electrolyte solid/liquid interface. To increase the capacitance of supercapacitors, transition metal oxides (manganese dioxide (MnO_2), ruthenium dioxide (RuO_2), etc.), transition metal nitrides (titanium nitride (TiN), ruthenium nitride (RuN), etc.), and conducting polymers (polypyrrole (PPy), polyaniline (PANI), etc.), are utilized to store energy via highly reversible surface redox reactions, and such an energy storage mechanism is called pseudocapacitance [23]. It is worth mentioning that printable methods are widely adopted in micro-supercapacitor fabrication for wearable and portable electronics, and thus the areal capacitance is one of the foremost performance factors [15]. Herein, versatile printable fabrication and modification methods aiming at increasing the areal capacitance of the supercapacitor devices will be introduced in the following paragraphs.

Carbon-based inks are the most popular materials for printable supercapacitors mainly due to the low resistance and high porosity, as well as good mechanical and electrochemical stability [102, 103]. Specific surfactants such as sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS) are usually added into inks to reduce the surface tension of the ink solvent and prevent the agglomeration of the ink solutes [27]. Moreover, conductive polymeric binders are utilized to tune the viscosity, surface tension, ink concentration and so forth, thus to meet the requirements of different printing methods [6, 6, 43, 104]. The high versatility of printing techniques is shown in Fig. 4. The electrode inks can be printed onto a large variety of substrates, including PET (Fig. 4(a)), printing paper (Fig. 4(b)), textile, etc. [43, 104–106]. Besides additive printing of carbon materials, high porosity can be produced by laser reduction of GO films or laser carbonization of polymer sheets [107], which also allows versatile and artistic pattern design (Fig. 4(c)). Ajayan's group found that GO films with water trapped between layers can serve as an electrode separator as well as an electrolyte, and a monolithic rGO-based supercapacitor was successfully demonstrated with laser-reduced patterning [98]. Apart from the printable

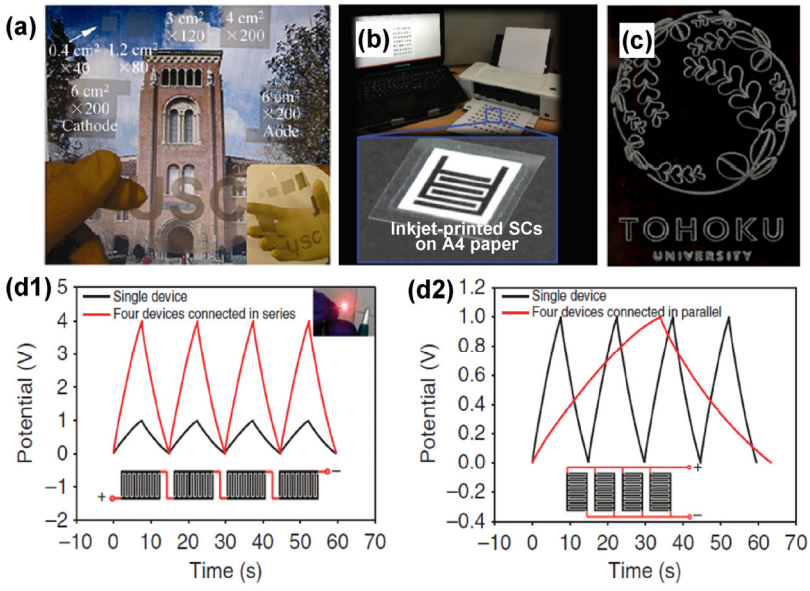

Figure 4 (a) Single-walled carbon nanotube films inkjet-printed on PET with different geometries and printing passes (reproduced with permission from Ref. [43], © Springer 2010). (b) All-inkjet-printed solid-state EDLC on printing paper (reproduced with permission from Ref. [106], © Royal Society of Chemistry 2016). (c) Pattern design demonstrated with laser carbonization (bright contrast) on dark color PI film using a blue-violet CW semiconductor laser with a wavelength of 405 nm (reproduced with permission from Ref. [107], © Royal Society of Chemistry 2016). (d) Facile circuit configurations of printable planar supercapacitors connected (d1) in series and (d2) in parallel (reproduced with permission from Ref. [97], © Nature Publishing Group 2013).

EDLCs mentioned above, pseudocapacitive materials were also explored for printing [108]. Moreover, the device configurations at the circuit level can be conveniently achieved to realize high operational voltage or adequate current output for practical applications, and can be further integrated with artistic pattern designs in a facile manner, as shown in Fig. 4(d) [97].

However, limited by the small surface area, most of the reported printable supercapacitors have relatively low normalized areal capacitance, generally less than 20 mF·cm^{-2} [15]. Thereby, several printable strategies have been proposed to enhance device capacitance, and the as-fabricated devices deliver competitive performance compared with commercial devices or those that are prepared via non-printing methods. One of the effective strategies is to construct electrodes with desirable nanostructures, which provide larger surface area for more charge storage and the well-controlled porosity for better ion diffusion and electron transport [109–113]. Zhu and co-workers demonstrated millimeter ultrathick electrodes with periodic macropores by 3D printing of formulated graphene aerogel, as shown in Fig. 5(a) [114]. Such an additive printing method enables the fabrication of high aspect ratio structures and precise control over porosity [27]. Moreover, such 3D networks also demonstrated high mechanical tolerance to realize long cycle stability. Thus, the achieved capacitance retention and power densities are superior to those values of bulk materials with similar dimensions [114].

It is also possible to combine printing techniques with conventional material deposition methods so as to fabricate high performance supercapacitors. For instance, Kaner's group utilized laser-scribing printing techniques to create highly porous rGO materials and an electrochemical deposition method to deposit large amounts of MnO_2 [58, 115]. The as-fabricated micro-supercapacitor achieves an impressively high areal capacitance of up to 400 mF·cm^{-2}, as shown in Fig. 5(b) [58]. Apart from construction of highly porous nanostructures, increasing the electrode density is another key factor to realize high normalized capacitance. Recently, Lin et al. reported planar supercapacitors with a minimum interspace of 5 μm between neighboring nanocoral-structured electrodes, which was realized by combination of inkjet printing and electrochemical depositions (Fig. 6(c)) [116]. The

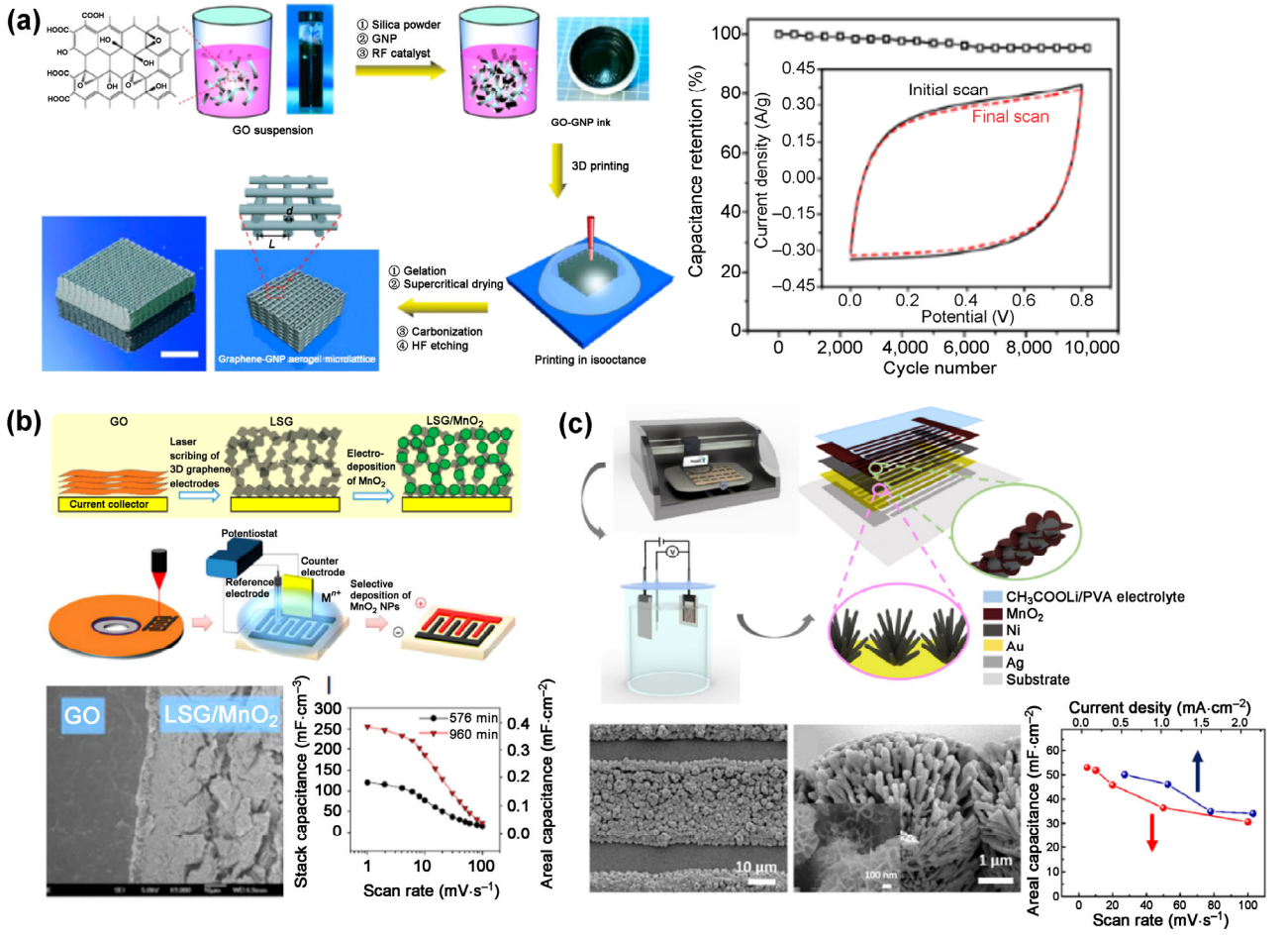

Figure 5 Printable fabrication of supercapacitors with improved performance. (a) Ultra-thick 3D electrodes with ordered architectures produced by 3D printing (reproduced with permission from Ref. [114], © American Chemical Society 2016). (b) Highly porous graphene electrodes prepared by laser writing for large active materials loading (reproduced with permission from Ref. [58], © National Academy of Sciences 2015). (c) Planar supercapacitors with nanocoral-structured electrodes fabricated by combining high resolution inkjet printing and electrochemical depositions (reproduced with permission from Ref. [116], © Wiley-VCH 2017).

as-fabricated supercapacitors with high electrode density, shortened ion diffusion lengths and hierarchical nanocoral structures, demonstrated a remarkable enhancement in both specific energy and power. Given the above, these printable fabrication strategies offer a promising future for fabrication of energy storage devices with reliable energy storage capacity, fast charging, long cycle life and high compatibility to be integrated with other kinds of electronic devices.

4.2 Rechargeable batteries

Compared with supercapacitors, rechargeable batteries possess higher energy density, more stable operation voltage and relatively lower self-discharging rate. Unlike supercapacitors that store energy via surface electrochemical activities, the energy storage or release in rechargeable batteries is accomplished with the process of ion intercalation/deintercalation into the bulk electrode. Such a process leads to multiple crystallographic phase changes of the active materials, conversion reaction and alloying/de-alloying processes. Among the variety of rechargeable batteries, lithium-ion batteries have been widely adopted as the main energy storage devices ever since they were first introduced in 1991 [23]. However, it is still a challenge to integrate rechargeable batteries into flexible and wearable electronics via a printable strategy due to their low tolerance of device deformation. Especially under bending conditions, electrolyte leakage and filament growth could result in a device failure.

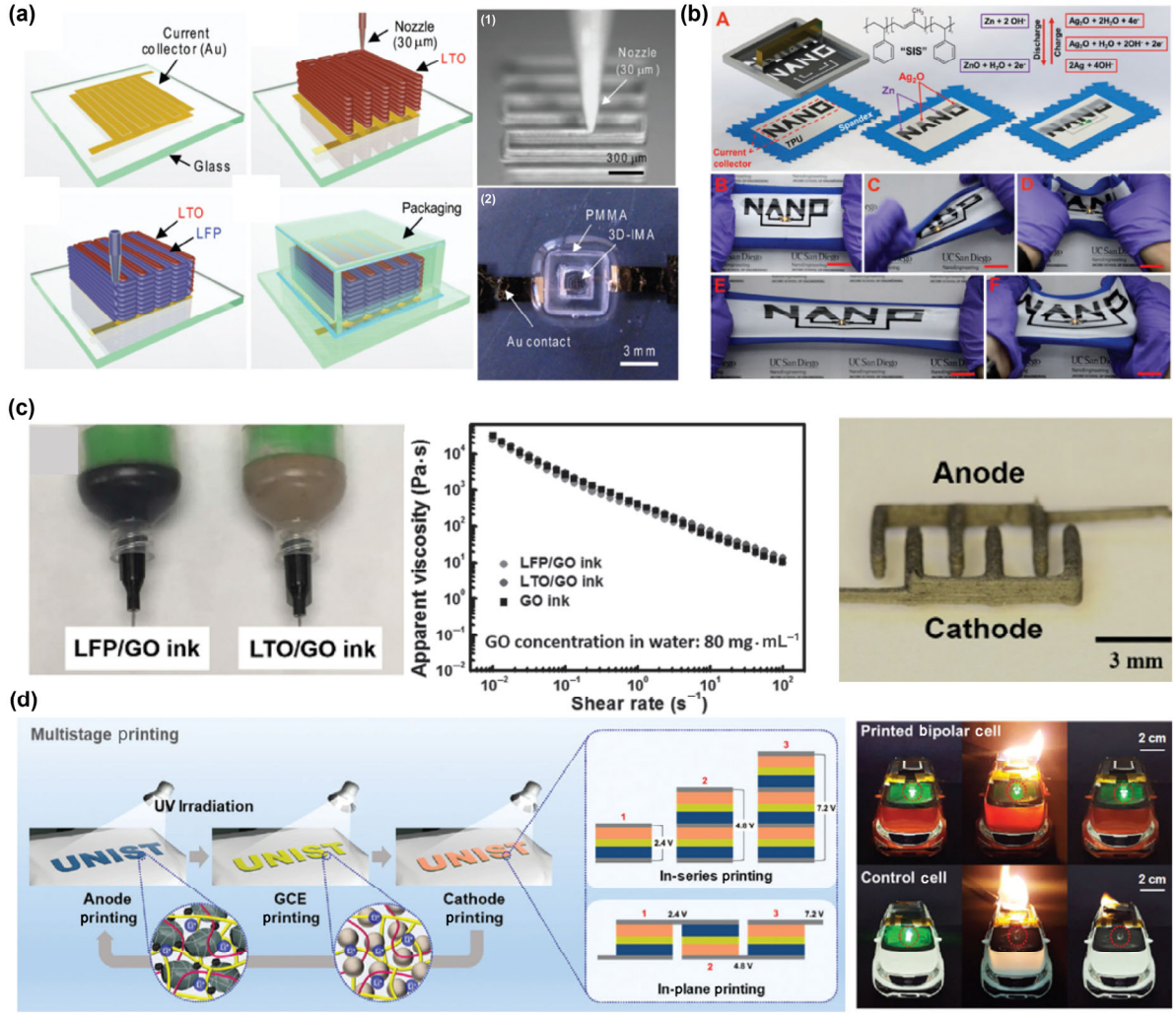

Figure 6 (a) The first demonstration of an integrated LIB by 3D printing (reproduced with permission from Ref. [52], © Wiley-VCH 2013). (b) Stretchable Zn-Ag_2O battery fabricated by screen printing (reproduced with permission from Ref. [122], © Wiley-VCH 2017). (c) Custom-made GO based conductive ink for direct 3D printable LIB (reproduced with permission from Ref. [123], © Wiley-VCH 2016). (d) All-solid-state LIB prepared by UV curing-assisted multistage printing with abuse tolerance (reproduced with permission from Ref. [126], © Royal Society of Chemistry 2017).

Research attempts to novel printable fabrication strategies and formulation of printable materials are introduced in the following paragraphs, while continuing efforts are required for performance enhancement, such as capability and cycling stability.

The first representative work on a printable lithium ion battery (LIB) was done by Sun and coworkers, as shown in Fig. 6(a) [52]. In this work, the main components of the micro batteries, including cathodes, anodes, electrolytes and encapsulation, were fabricated by 3D printing. By tuning the rheological properties of inks, such as by active materials' ratio, additive selections and concentrations, it is possible to realize filament formation, achieve quick solidification and maintain structure stability during material stacking. As a direct consequence, a lithium iron phosphate (LFP) cathode and a lithium titanate (LTO) anode were precisely printed. Such a printing process enables the construction of high aspect ratio 3D electrodes within a small footprint area, which is also a promising strategy to improve the energy storage capacity [117, 118]. Apart from LIBs, zinc-based batteries, which utilized an aqueous electrolyte to avoid potential flammability issues of the LIB, have also been fabricated via printing methods [119–121]. Meng's group successfully demonstrated an all-printed and

stretchable planar zinc-silver oxide (Zn-Ag_2O) battery, as shown in Fig. 6(b) [122]. In this work, polystyrene-block-polyisoprene-block-polystyrene (SIS) as hyperelastic binder was introduced to prepare inks with high mechanical tolerance. The as-printed aqueous rechargeable Zn batteries achieved a reversible capacity density of around 2.5 $mAh \cdot cm^{-2}$ at a discharge current of 3 $mA \cdot cm^{-2}$, which is currently the highest value among intrinsically stretchable batteries. Moreover, the device retained considerable performance undergoing stretching and twisting. Such custom-made inks with high stress-enduring property provide a promising strategy to develop printable and stretchable electronics for wearable applications.

Though polymer binders contribute to the increased mechanical robustness of printed devices, it might compromise the conductivity of the electrodes in the meantime. To solve this problem, Fu and co-workers modified the electrode inks by mixing active materials with GO sheets, which would be further reduced to conductive and porous rGO [123]. Thus, concentrated inks with highly conductive and proper rheological properties were synthesized for direct electrode printing. Notably, GO sheet alignment by shear stress was found along the extrusion direction, and thus, a porous network was formed to provide continuous electron pathways and ion diffusion channels, leading to significantly improved electrochemical performances. Without extra processing for current collector patterning, such micro batteries can be directly constructed onto a variety of substrates (Fig. 6(c)). Recently, lithium-sulfur cathodes fabricated by inkjet printing were also reported. By mixing single-wall carbon nanotubes and conductive straight-chain sulfur as printable inks, the as-fabricated microcathodes delivered a capacity of around 800 $mAh \cdot g^{-1}$, and such a value is the highest among batteries fabricated with printing techniques [124]. Apart from active materials, electrolytes with uniform porosity and remarkable electrochemical/mechanical/thermal stability are also critical requirements for high performance batteries [112]. By adding aluminum oxide (Al_2O_3) fillers into inks, Blake et al. generated polymer electrolyte with a controllable and uniform porous matrix by 3D printing for LIB applications. It was demonstrated that such porous electrolytes exhibited better wetting characteristics and enhanced thermal stability as compared to non-porous electrolytes [112]. Research attention was also devoted to the safety failures of LIBs that use flammable electrolytes [125]. For instance, Lee's group recently developed a new class of flexible bipolar LIBs with exceptional abuse tolerance [126]. As shown in Fig. 6(d), the all-solid-state LIBs were fabricated via a UV curing-assisted multistage printing approach utilizing a novel flexible and nonflammable gel electrolyte consisting of sebaconitrile (SBN)-based electrolyte and a semi-interpenetrating polymer network skeleton. Compared with traditional LIB using inorganic electrolytes, the as-fabricated LIBs also demonstrated superior safety robustness when exposed to flame or even after they were cut in half. However, such printable inks with large aspect ratio fillers or sheets can only be adapted for large printing nozzles or via screen printing methods, which still pose challenges for further performance enhancements and fabrication versatility [26].

5 Printable fabrication of self-powered energy sources

The integration of energy conversion and storage devices into a self-powered energy source is one of the ultimate solutions to meet the demand for next generation wearable and portable electronics. Prototypes of such energy systems have been demonstrated successfully on rigid substrates and textiles, etc. [14]. The emerging printing techniques provide alternative and facile routes for the monolithic fabrication and seamless connection of two different energy devices, which will be reviewed in this section.

5.1 Prototype integrated self-powered energy sources

One of the ultimate solutions to meet the demands of wearable and portable electronics is to integrate energy conversion and storage devices into an independent power source [13, 127]. Several types of integrated systems have been demonstrated, such as photovoltaics-battery [128, 129], photovoltaics-supercapacitor [130–132], nanogenerator-supercapacitor [133], etc. Although there is a lack of standards for system performance evaluation, energy conversion and storage efficiency and cycling stability are the most

important figures-of-merit among all the characteristics. To achieve reliable functionality and considerable performance of such self-powered energy sources, stable functionality of the individual devices, parameter matching of two different devices and robust integration are essential [134]. For a photo-charging integrated energy source, the energy conversion and storage efficiency (η) can be calculated following Eq. (1)

$$\eta = \frac{E}{P \cdot A \cdot t} \times 100\% \quad (1)$$

where E, P, A and t are discharge energy of the energy storage device (mWh), light power density ($mW \cdot cm^{-2}$), effective photovoltaic device area (cm^2) and photo-charging time (h), respectively [14, 135].

The system operation principle of such integrated self-powered energy sources can be illustrated by the schematic diagram of a LIB photo-charging by a perovskite solar cell, as shown in Fig. 7(a) [135]. Under solar radiation, electron/hole pairs are generated in the perovskite layer in the solar cell and transported to the anode and cathode, respectively, thus generating electric current flow. Such photo-generated current can either power the energy consumption devices, or be stored in the LIB and release the energy when necessary.

Apart from the integration of two energy devices via external connection to realize robust monolithic integration, one of the widely employed integration strategies is stacked architectures with one common electrode, as shown in Fig. 7(b) [136]. The as-fabricated integrated energy source contains a layer of gold as a shared electrode. Such device architecture can be applied onto both rigid and flexible substrates [137, 138].

Another facile integration approach is utilizing conductive fibers as the common electrodes to connect the different devices, which has been widely demonstrated for further integration into wearable systems [139–141]. As shown in Fig. 7(c), Bae and co-workers reported for the first time a prototype integrating hybrid energy conversion devices, solar cells and a nanogenerator, together with a supercapacitor as the energy storage device [133]. The devices are fabricated using ZnO nanowires and graphene on a single poly(methyl methacrylate) (PMMA) fiber coated with Au, which served as common electrodes. Simultaneous energy harvesting from both solar and mechanical energies was realized.

However, the fabrication of integrated energy systems is still in the early stage of research. It relies on the stability of individual power supply devices, and considerable technical problems might be further introduced during the integrations. Therefore, it is even challenging to realize scalable fabrication of such self-powered energy sources by printing techniques, which will be further discussed.

5.2 Research advances in printable integrated self-powered energy sources

Due to the challenges mentioned in the previous

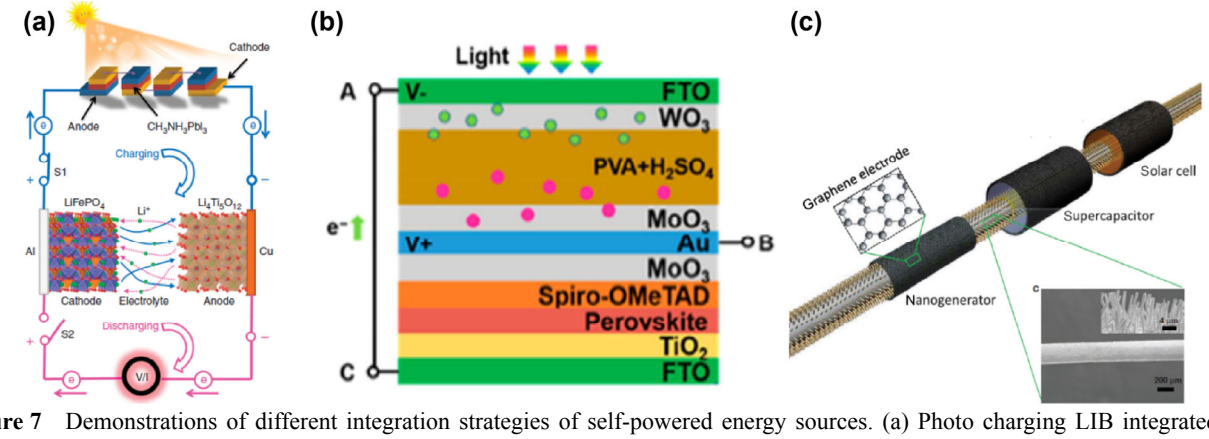

Figure 7 Demonstrations of different integration strategies of self-powered energy sources. (a) Photo charging LIB integrated with external connections (reproduced with permission from Ref. [135], © Nature Publishing Group 2015). (b) A perovskite solar cell integrated with supercapacitor stacked configuration with Au as common electrode (reproduced with permission from Ref. [136], © American Chemical Society 2016). (c) Integrated DSSC, nanogenerator and supercapacitor with single fiber as common electrode (reproduced with permission from Ref. [133], © Wiley-VCH 2011).

sections, research progress in printable fabrication of integrated systems are still in an infancy stage. Xia and co-workers innovatively combined a printable PVSC, similar to the devices that have been discussed in Section 3.1, and an electrochromic battery with WO_3 nanowires as anode materials and NiO/rGO as cathodes. Thus, the charging status can be indicated by the color variation and demonstrates its potential application in smart windows [142]. However, the integration of the two devices relies on external connection which introduces extra resistance into the whole system and is generally not preferable in portable and wearable electronics.

Recently, Lee's group has successfully fabricated a monolithically integrated energy source consisting of crystalline Si (c-Si) photovoltaics (SiPV) and a LIB energy source, as shown in Figs. 8(a) and 8(b) [13]. The all-solid-stage bipolar LIBs were directly fabricated onto the Al electrode of a c-Si PV module in a UV assisted in-series screen printing process, and thus seamless integration was realized (Fig. 8(c)). The entire SiPV-LIB unit was then well-packaged into a thin panel (Fig. 8(d)) and realized a photo-electric conversion and storage efficiency of up to 7.61%, which showed remarkable enhancement over previous works. Besides, the adoption of a c-Si PV and solid-state electrolyte contributed to the thermal stability of the entire system with over 95% capacity retention after 100 cycles at 60 ℃, as shown in Figs. 8(e) and 8(f). The device structural design and fabrication process shed light on the development of printable integrated self-powered energy sources.

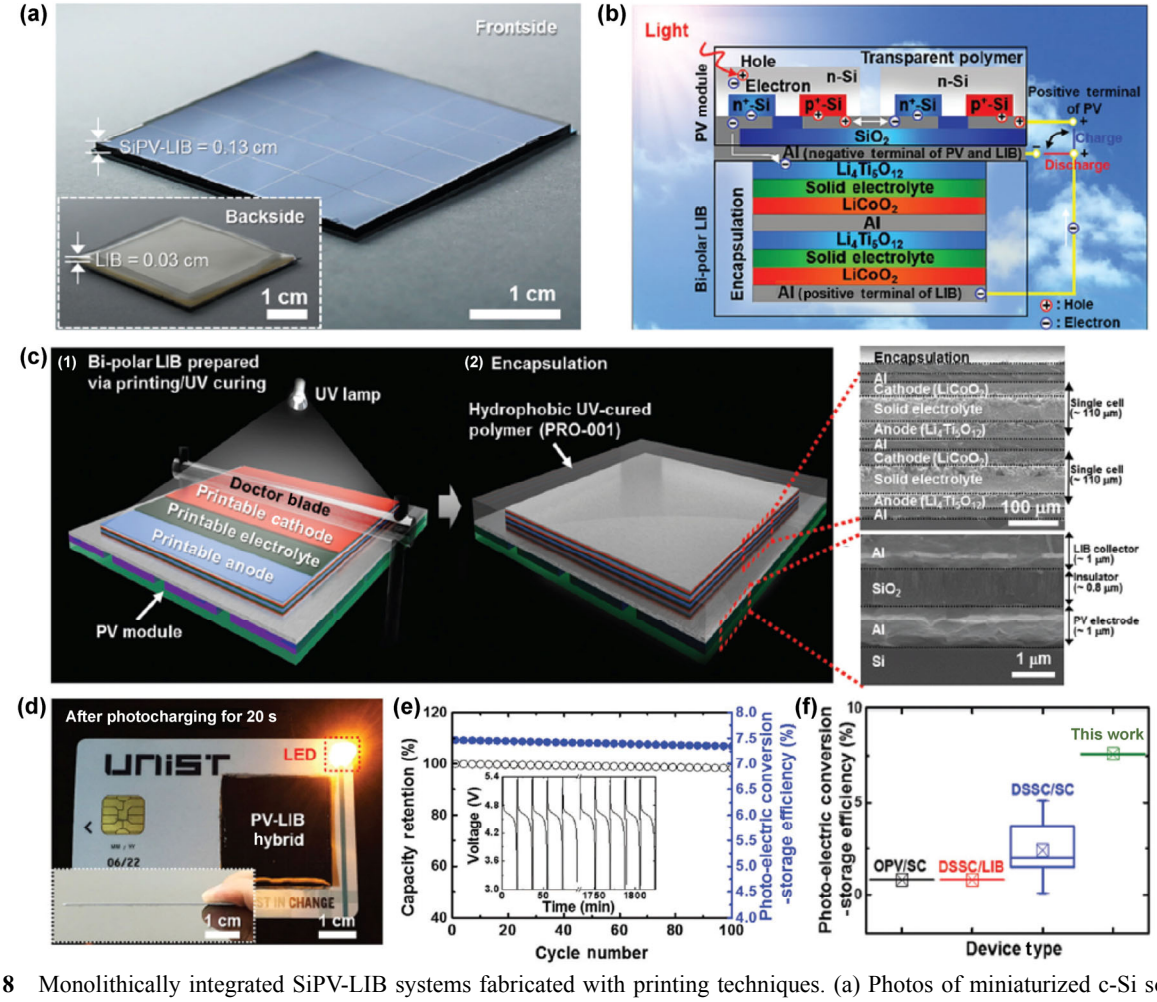

Figure 8 Monolithically integrated SiPV-LIB systems fabricated with printing techniques. (a) Photos of miniaturized c-Si solar cells array. (b) Schematic diagrams of SiPV-LIB system. (c) Solid-state LIBs fabricated directly on a c-Si panel in a UV-assisted screen-printing method and corresponding cross-sectional SEM image. (d) Photos of fully packaged SiPV-LIBs lighting up LED. (e) Cycling stability and (f) performance enhancement. Reproduced with permission from Ref. [13], © Royal Society of Chemistry 2017.

To the best of our knowledge, fully printable fabrication of energy systems with high integrity is still challenging, and no prototype has been demonstrated yet. However, printing techniques provide promising routes to integrate different devices with their pattern versatility. Also, the scalability of printing methods will no doubt benefit scalable fabrication of such integrated self-powered energy sources, to provide infinite energy for ubiquitous electronics.

6 Conclusions and prospects

Printable techniques hold promising potency for fabrication of power supply devices with practical scalability and versatility, especially for applications in wearable and portable electronics. In this review, various characteristics of different printing techniques, which are commonly employed in fabrication of printable power supply devices, are summarized. Research advances in device construction and performance enhancement attributed to the unique properties of nanomaterials are highlighted. The attractive properties of printable fabrication methods are illustrated, and the strategies for further improvements on energy conversion efficiency, energy storage capability and device integrity, are discussed. In addition to a brief review over integrated self-powered systems, progress in printable fabrication and integration of different energy devices into self-powered energy sources are also introduced, which is highly desirable for wearable and portable electronic devices.

It is obvious that printable methods provide innovative routes for fabrication of a variety of electronics with research advances in printing techniques, materials engineering and device structure revolutions. However, there are still several challenges to be addressed: 1) For practical application, it is essential that the developed printing methods are compatible with manufacturing processes, which require high scalability and throughput. Therefore, modifications on device architectures and selection of printable materials are critical. For instance, a planar device configuration that consists of a single layer is highly preferred in printable fabrications. It reduces the complexity of printing layer-by-layer stacked architectures and avoids the risk of solvent dissolution between layers or potential solvent attacks to the deposited materials. Moreover, materials that contain high aspect ratio fillers or flakes tend to aggregate easily and can only flow through large nozzles, which limits the variety of printable materials and lowers the fabrication efficiency due to nozzle clogging issues. 2) With limited choice on printable materials, active material mass loading and surface engineering capability of printing methods are still lacking in competitiveness with electrochemical deposition, evaporation and sputtering, etc. Therefore, the performances of printable devices are inferior to the ones that are fabricated by those conventional techniques. Especially for miniaturized electronics, one of the key factors to enhance the normalized energy harvesting and storage capability is to realize high printing resolution. Thus, dedicated research efforts should be invested on the modification of printable ink with proper viscosity, hydrophilic/hydrophobic properties and so on, to realize precise patterning together with high mass density loading on a variety of substrates. Apart from printing resolution, well-controlled surface morphology is another key factor. Particularly, compact and smooth surfaces are critical for solar cells, while highly porous nanostructures with large surface area are preferable for nanogenerators, BFCs, supercapacitors and batteries. Therefore, innovative printing procedures with combinations of appropriate printing techniques, including the printing techniques discussed above and other printing methods, such as roll-to-roll printing [24, 40], even with assistance of conventional techniques are preferred. 3) Up to now, it is still challenging to fabricate the entire functionalized devices or integrated systems via printing procedures. To meet the demand of next generation wearable devices, it is highly desirable to realize fully printable fabrication of power supply devices, with merits of design versatility and respectable performance, as well as robust and seamless integrity.

Overall, rapid research progress on printable electronics based on nanomaterials, especially power devices and systems, have been witnessed in recent years. And the innovatively developed printable fabrication methods demonstrate remarkable scalability and desirable fabrication versatility, which are essential

to meet the demands of next generation wearable and portable electronics. However, research in this field is still in an infancy stage and several challenges need to be addressed in order to realize printable integrated self-powered systems with remarkable performance and attractive attributes, such as self-healing [104], shape memory or electrochromic properties [143, 144], which are also desirable for wearable and portable systems.

Acknowledgements

The authors acknowledge financial support from National Natural Science Foundation of China (No. 51672231), Hong Kong Research Grant Council (General Research Fund Project No. 16237816), and Center for 1D/2D Quantum Materials and State Key Laboratory on Advanced Displays and Optoelectronics at HKUST.

References

[1] Gao, W.; Emaminejad, S.; Nyein, H. Y. Y.; Challa, S.; Chen, K.; Peck, A.; Fahad, H. M.; Ota, H.; Shiraki, H.; Kiriya, D. et al. Fully integrated wearable sensor arrays for multiplexed *in situ* perspiration analysis. *Nature* **2016**, *529*, 509–514.

[2] Jia, W. Z.; Wang, X.; Imani, S.; Bandodkar, A. J.; Ramírez, J.; Mercier, P. P.; Wang, J. Wearable textile biofuel cells for powering electronics. *J. Mater. Chem. A* **2014**, *2*, 18184–18189.

[3] Honda, W.; Harada, S.; Arie, T.; Akita, S.; Takei, K. Wearable, human-interactive, health-monitoring, wireless devices fabricated by macroscale printing techniques. *Adv. Funct. Mater.* **2014**, *24*, 3299–3304.

[4] Son, D.; Lee, J.; Qiao, S. T.; Ghaffari, R.; Kim, J.; Lee, J. E.; Song, C.; Kim, S. J.; Lee, D. J.; Jun, S. W. et al. Multifunctional wearable devices for diagnosis and therapy of movement disorders. *Nat. Nanotechnol.* **2014**, *9*, 397–404.

[5] Wang, Z. L.; Song, J. H. Piezoelectric nanogenerators based on zinc oxide nanowire arrays. *Science* **2006**, *312*, 242–246.

[6] Kim, J.; Kumar, R.; Bandodkar, A. J.; Wang, J. Advanced materials for printed wearable electrochemical devices: A review. *Adv. Electron. Mater.* **2017**, *3*, 1600260.

[7] Wang, Z. L. Towards self-powered nanosystems: From nanogenerators to nanopiezotronics. *Adv. Funct. Mater.* **2008**, *18*, 3553–3567.

[8] Leung, S. F.; Tsui, K. H.; Lin, Q. F.; Huang, H. T.; Lu, L. F.; Shieh, J. M.; Shen, C. H.; Hsu, C. H.; Zhang, Q. P.; Li, D. D. et al. Large scale, flexible and three-dimensional quasi-ordered aluminum nanospikes for thin film photovoltaics with omnidirectional light trapping and optimized electrical design. *Energy Environ. Sci.* **2014**, *7*, 3611–3616.

[9] Lin, Q. F.; Lu, L. F.; Tavakoli, M. M.; Zhang, C.; Lui, G. C.; Chen, Z.; Chen, X. Y.; Tang, L.; Zhang, D. Q.; Lin, Y. J. et al. High performance thin film solar cells on plastic substrates with nanostructure-enhanced flexibility. *Nano Energy* **2016**, ***22***, 539–547.

[10] Fan, F. R.; Tian, Z. Q.; Wang, Z. L. Flexible triboelectric generator. *Nano Energy* **2012**, *1*, 328–334.

[11] Sakai, H.; Nakagawa, T.; Tokita, Y.; Hatazawa, T.; Ikeda, T.; Tsujimura, S.; Kano, K. A high-power glucose/oxygen biofuel cell operating under quiescent conditions. *Energy Environ. Sci.* **2009**, *2*, 133–138.

[12] Jia, W. Z.; Valdés-Ramírez, G.; Bandodkar, A. J.; Windmiller, J. R.; Wang, J. Epidermal biofuel cells: Energy harvesting from human perspiration. *Angew. Chem., Int. Ed.* **2013**, *52*, 7233–7236.

[13] Um, H. D.; Choi, K. H.; Hwang, I.; Kim, S. H.; Seo, K.; Lee, S. Y. Monolithically integrated, photo-rechargeable portable power sources based on miniaturized Si solar cells and printed solid-state lithium-ion batteries. *Energy Environ. Sci.* **2017**, *10*, 931–940.

[14] Liu, R. Y.; Liu, Y. Q.; Zou, H. Y.; Song, T.; Sun, B. Q. Integrated solar capacitors for energy conversion and storage. *Nano Res.* **2017**, *10*, 1545–1559.

[15] Kyerematen, N. A.; Brousse, T.; Pech, D. Microsuper-capacitors as miniaturized energy-storage components for on-chip electronics. *Nat. Nanotechnol.* **2017**, *12*, 7–15.

[16] Pech, D.; Brunet, M.; Taberna, P. L.; Simon, P.; Fabre, N.; Mesnilgrente, F.; Conédéra, V.; Durou, H. Elaboration of a microstructured inkjet-printed carbon electrochemical capacitor. *J. Power Sources* **2010**, *195*, 1266–1269.

[17] Gu, L. L.; Tavakoli, M. M.; Zhang, D. Q.; Zhang, Q. P.; Waleed, A.; Xiao, Y. Q.; Tsui, K. H.; Lin, Y. J.; Liao, L.; Wang, J. N. et al. 3D arrays of 1024-pixel image sensors based on lead halide perovskite nanowires. *Adv. Mater.* **2016**, *28*, 9713–9721.

[18] Lin, Q. F.; Sarkar, D.; Lin, Y. J.; Yeung, M.; Blankemeier, L.; Hazra, J.; Wang, W.; Niu, S. Y.; Ravichandran, J.; Fan, Z. Y. et al. Scalable indium phosphide thin-film nanophotonics platform for photovoltaic and photoelectrochemical devices. *ACS Nano* **2017**, *11*, 5113–5119.

[19] Gao, Y.; Jin, H. Y.; Lin, Q. F.; Li, X.; Tavakoli, M. M.; Leung, S. F.; Tang, W. M.; Zhou, L. M.; Chan, H. L. W.; Fan, Z. Y. Highly flexible and transferable supercapacitors

with ordered three-dimensional MnO_2/Au/MnO_2 nanospike arrays. *J. Mater. Chem. A* **2015**, *3*, 10199–10204.

[20] Fan, Z. Y.; Ruebusch, D. J.; Rathore, A. A.; Kapadia, R.; Ergen, O.; Leu, P. W.; Javey, A. Challenges and prospects of nanopillar-based solar cells. *Nano Res.* **2009**, *2*, 829–843.

[21] Cao, X.; Chen, H. T.; Gu, X. F.; Liu, B. L.; Wang, W. L.; Cao, Y.; Wu, F. Q.; Zhou, C. W. Screen printing as a scalable and low-cost approach for rigid and flexible thin-film transistors using separated carbon nanotubes. *ACS Nano* **2014**, *8*, 12769–12776.

[22] Singh, M.; Haverinen, H. M.; Dhagat, P.; Jabbour, G. E. Inkjet printing—Process and its applications. *Adv. Mater.* **2010**, *22*, 673–685.

[23] Li, L.; Wu, Z.; Yuan, S.; Zhang, X. B. Advances and challenges for flexible energy storage and conversion devices and systems. *Energy Environ. Sci.* **2014**, *7*, 2101–2122.

[24] Yu, X.; Marks, T. J.; Facchetti, A. Metal oxides for optoelectronic applications. *Nat. Mater.* **2016**, *15*, 383–396.

[25] Beidaghi, M.; Gogotsi, Y. Capacitive energy storage in micro-scale devices: Recent advances in design and fabrication of micro-supercapacitors. *Energy Environ. Sci.* **2014**, *7*, 867–884.

[26] Zhu, C.; Liu, T. Y.; Qian, F.; Chen, W.; Chandrasekaran, S.; Yao, B.; Song, Y.; Duoss, E. B.; Kuntz, J. D.; Spadaccini, C. M. et al. 3D printed functional nanomaterials for electrochemical energy storage. *Nano Today* **2017**, *15*, 107–120.

[27] Zhang, F.; Wei, M.; Viswanathan, V. V.; Swart, B.; Shao, Y. Y.; Wu, G.; Zhou, C. 3D printing technologies for electrochemical energy storage. *Nano Energy* **2017**, *40*, 418–431.

[28] Noh, Y. Y.; Zhao, N.; Caironi, M.; Sirringhaus, H. Downscaling of self-aligned, all-printed polymer thin-film transistors. *Nat. Nanotechnol.* **2007**, *2*, 784–789.

[29] Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. High-resolution inkjet printing of all-polymer transistor circuits. *Science* **2000**, *290*, 2123–2126.

[30] Sekitani, T.; Noguchi, Y.; Zschieschang, U.; Klauk, H.; Someya, T. Organic transistors manufactured using inkjet technology with subfemtoliter accuracy. *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 4976–4980.

[31] Torrisi, F.; Hasan, T.; Wu, W. P.; Sun, Z. P.; Lombardo, A.; Kulmala, T. S.; Hsieh, G.; Jung, S.; Bonaccorso, F.; Paul, P. J. et al. Inkjet-printed graphene electronics. *ACS Nano* **2012**, *6*, 2992–3006.

[32] Azzellino, G.; Grimoldi, A.; Binda, M.; Caironi, M.; Natali, D.; Sampietro, M. Fully inkjet-printed organic photodetectors with high quantum yield. *Adv. Mater.* **2013**, *25*, 6829–6833.

[33] Liu, X.; Gu, L. L.; Zhang, Q. P.; Wu, J. Y.; Long, Y. Z.; Fan, Z. Y. All-printable band-edge modulated ZnO nanowire photodetectors with ultra-high detectivity. *Nat. Commun.* **2014**, *5*, 4007.

[34] Ota, H.; Chao, M. H.; Gao, Y. J.; Wu, E.; Tai, L. C.; Chen, K.; Matsuoka, Y.; Iwai, K.; Fahad, H. M.; Gao, W. et al. 3D printed "Earable" smart devices for real-time detection of core body temperature. *ACS Sens.* **2017**, *2*, 990–997.

[35] Rim, Y. S.; Bae, S. H.; Chen, H. J.; De Marco, N.; Yang, Y. Recent progress in materials and devices toward printable and flexible sensors. *Adv. Mater.* **2016**, *28*, 4415–4440.

[36] Chen, K.; Gao, W.; Emaminejad, S.; Kiriya, D.; Ota, H.; Nyein, H. Y. Y.; Takei, K.; Javey, A. Printed carbon nanotube electronics and sensor systems. *Adv. Mater.* **2016**, *28*, 4397–4414.

[37] Dua, V.; Surwade, S. P.; Ammu, S.; Agnihotra, S. R.; Jain, S.; Roberts, K. E.; Park, S.; Ruoff, R. S.; Manohar, S. K. All-organic vapor sensor using inkjet-printed reduced graphene oxide. *Angew. Chem.* **2010**, *122*, 2200–2203.

[38] Jang, J.; Ha, J.; Cho, J. Fabrication of water-dispersible polyaniline-poly (4-styrenesulfonate) nanoparticles for inkjet-printed chemical-sensor applications. *Adv. Mater.* **2007**, *19*, 1772–1775.

[39] Nomura, K.; Kaji, R.; Iwata, S.; Otao, S.; Imawaka, N.; Yoshino, K.; Mitsui, R.; Sato, J.; Takahashi, S.; Nakajima, S. et al. A flexible proximity sensor formed by duplex screen/screen-offset printing and its application to non-contact detection of human breathing. *Sci. Rep.* **2016**, *6*, 19947.

[40] Khan, S.; Lorenzelli, L.; Dahiya, R. S. Technologies for printing sensors and electronics over large flexible substrates: A review. *IEEE Sens. J.* **2015**, *15*, 3164–3185.

[41] Kuroda Electric Home Page. http://www.kuroda-electric.eu/Ultra-Fine-Pattern-Screen-Printing (accessed Feb 2, 2018).

[42] Jost, K.; Stenger, D.; Perez, C. R.; McDonough, J. K.; Lian, K.; Gogotsi, Y.; Dion, G. Knitted and screen printed carbon-fiber supercapacitors for applications in wearable electronics. *Energy Environ. Sci.* **2013**, *6*, 2698–2705.

[43] Chen, P.; Chen, H. T.; Qiu, J.; Zhou, C. W. Inkjet printing of single-walled carbon nanotube/RuO_2 nanowire supercapacitors on cloth fabrics and flexible substrates. *Nano Res.* **2010**, *3*, 594–603.

[44] de Gans, B. J.; Duineveld, P. C.; Schubert, U. S. Inkjet printing of polymers: State of the art and future developments. *Adv. Mater.* **2004**, *16*, 203–213.

[45] Kumar, B.; Tan, H. S.; Ramalingam, N.; Mhaisalkar, S. G. Integration of ink jet and transfer printing for device fabrication using nanostructured materials. *Carbon* **2009**, *47*, 321–324.

[46] Kawahara, Y.; Hodges, S.; Cook, B. S.; Zhang, C.; Abowd, G. D. Instant inkjet circuits: Lab-based inkjet printing to support rapid prototyping of UbiComp devices. In *Proceedings of the 2013 ACM International Joint Conference on Pervasive and Ubiquitous Computing*, Zurich, Switzerland, 2013, pp 363–372.

[47] Siegel, A. C.; Phillips, S. T.; Dickey, M. D.; Lu, N. S.; Suo, Z. G.; Whitesides, G. M. Foldable printed circuit boards on paper substrates. *Adv. Funct. Mater.* **2010**, *20*, 28–35.

[48] Yang, C.; Cui, X. Y.; Zhang, Z. X.; Chiang, S. W.; Lin, W.; Duan, H.; Li, J.; Kang, F. Y.; Wong, C. P. Fractal dendrite-based electrically conductive composites for laser-scribed flexible circuits. *Nat. Commun.* **2015**, *6*, 8150.

[49] Hoth, C. N.; Choulis, S. A.; Schilinsky, P.; Brabec, C. J. High photovoltaic performance of inkjet printed polymer: Fullerene blends. *Adv. Mater.* **2007**, *19*, 3973–3978.

[50] Kim, K.; Zhu, W.; Qu, X.; Aaronson, C.; McCall, W. R.; Chen, S. C.; Sirbuly, D. J. 3D optical printing of piezoelectric nanoparticle–polymer composite materials. *ACS Nano* **2014**, *8*, 9799–9806.

[51] Fu, K.; Yao, Y. G.; Dai, J. Q.; Hu, L. B. Progress in 3D printing of carbon materials for energy-related applications. *Adv. Mater.* **2017**, *29*, 1603486.

[52] Sun, K.; Wei, T. S.; Ahn, B. Y.; Seo, J. Y.; Dillon, S. J.; Lewis, J. A. 3D printing of interdigitated Li-ion microbattery architectures. *Adv. Mater.* **2013**, *25*, 4539–4543.

[53] Zhang, B.; Seong, B.; Nguyen, V.; Byun, D. 3D printing of high-resolution PLA-based structures by hybrid electrohydrodynamic and fused deposition modeling techniques. *J. Micromech. Microeng.* **2016**, *26*, 025015.

[54] Zhu, C.; Han, T. Y. J.; Duoss, E. B.; Golobic, A. M.; Kuntz, J. D.; Spadaccini, C. M.; Worsley, M. A. Highly compressible 3D periodic graphene aerogel microlattices. *Nat. Commun.* **2015**, *6*, 6962.

[55] Zhang, Y. L.; Guo, L.; Wei, S.; He, Y. Y.; Xia, H.; Chen, Q. D.; Sun, H. B.; Xiao, F. S. Direct imprinting of microcircuits on graphene oxides film by femtosecond laser reduction. *Nano Today* **2010**, *5*, 15–20.

[56] Strong, V.; Dubin, S.; El-Kady, M. F.; Lech, A.; Wang, Y.; Weiller, B. H.; Kaner, R. B. Patterning and electronic tuning of laser scribed graphene for flexible all-carbon devices. *ACS Nano* **2012**, *6*, 1395–1403.

[57] Huang, H. C.; Chung, C. J.; Hsieh, C. T.; Kuo, P. L.; Teng, H. Laser fabrication of all-solid-state microsupercapacitors with ultrahigh energy and power based on hierarchical pore carbon. *Nano Energy* **2016**, *21*, 90–105.

[58] El-Kady, M. F.; Ihns, M.; Li, M. P.; Hwang, J. Y.; Mousavi, M. F.; Chaney, L.; Lech, A. T.; Kaner, R. B. Engineering three-dimensional hybrid supercapacitors and microsupercapacitors for high-performance integrated energy storage. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 4233–4238.

[59] Torrisi, F.; Coleman, J. N. Electrifying inks with 2D materials. *Nat. Nanotechnol.* **2014**, *9*, 738–739.

[60] Cao, L. J.; Yang, S. B.; Gao, W.; Liu, Z.; Gong, Y. J.; Ma, L. L.; Shi, G.; Lei, S. D.; Zhang, Y H.; Zhang, S. T. et al. Direct laser-patterned micro-supercapacitors from paintable MoS_2 films. *Small* **2013**, *9*, 2905–2910.

[61] Jung, M.; Kim, J.; Noh, J.; Lim, N.; Lim, C.; Lee, G.; Kim, J.; Kang, H.; Jung, K.; Leonard, A. D. et al. All-printed and roll-to-roll-printable 13.56-MHz-operated 1-bit RF tag on plastic foils. *IEEE Trans. Electron Devices* **2010**, *57*, 571–580.

[62] Yang, L.; Rida, A.; Vyas, R.; Tentzeris, M. M. RFID tag and RF structures on a paper substrate using inkjet-printing technology. *IEEE Trans. Microw. Theory Tech.* **2007**, *55*, 2894–2901.

[63] Izumi, K.; Yoshida, Y.; Tokito, S. Improved fine layer patterning using soft blanket gravure printing technology. *Flex. Print. Electron.* **2018**, *3*, 015011.

[64] Sheng, X.; Bower, C. A.; Bonafede, S.; Wilson, J. W.; Fisher, B.; Meitl, M.; Yuen, H.; Wang, S. D.; Shen, L.; Banks, A. R. et al. Printing-based assembly of quadruple-junction four-terminal microscale solar cells and their use in high-efficiency modules. *Nat. Mater.* **2014**, *13*, 593–598.

[65] Hoey, J. M.; Lutfurakhmanov, A.; Schulz, D. L.; Akhatov, I. S. A review on aerosol-based direct-write and its applications for microelectronics. *J. Nanotechnol.* **2012**, *2012*, Article ID 324380.

[66] Seifert, T.; Sowade, E.; Roscher, F.; Wiemer, M.; Gessner, T.; Baumann, R. R. Additive manufacturing technologies compared: Morphology of deposits of silver ink using inkjet and aerosol jet printing. *Ind. Eng. Chem. Res.* **2015**, *54*, 769–779.

[67] Bag, S.; Deneault, J. R.; Durstock, M. F. Aerosol-jet-assisted thin-film growth of $CH_3NH_3PbI_3$ perovskites—A means to achieve high quality, defect-free films for efficient solar cells. *Adv. Energy Mater.* **2017**, *7*, 1701151.

[68] Chen, W.; Wu, Y. Z.; Yue, Y. F.; Liu, J.; Zhang, W. J.; Yang, X. D.; Chen, H.; Bi, E. B.; Ashraful, I.; Grätzel, M. et al. Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science* **2015**, *350*, 944–948.

[69] Shaheen, S. E.; Radspinner, R.; Peyghambarian, N.; Jabbour, G. E. Fabrication of bulk heterojunction plastic solar cells by screen printing. *Appl. Phys. Lett.* **2001**, *79*, 2996–2998.

[70] Guo, Q. J.; Kim, S. J.; Kar, M.; Shafarman, W. N.; Birkmire, R. W.; Stach, E. A.; Agrawal, R.; Hillhouse, H. W. Development of $CuInSe_2$ nanocrystal and nanoring inks for

low-cost solar cells. *Nano Lett.* **2008**, *8*, 2982–2987.

[71] Panthani, M. G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. Synthesis of $CuInS_2$, $CuInSe_2$, and Cu (In_xGa_{1-x}) Se_2 (CIGS) nanocrystal "inks" for printable photovoltaics. *J. Am. Chem. Soc.* **2008**, *130*, 16770–16777.

[72] Kovalenko, M. V. Opportunities and challenges for quantum dot photovoltaics. *Nat. Nanotechnol.* **2015**, *10*, 994–997.

[73] Guo, F.; Li, N.; Radmilović, V. V.; Radmilović, V. R.; Turbiez, M.; Spiecker, E.; Forberich, K.; Brabec, C. J. Fully printed organic tandem solar cells using solution-processed silver nanowires and opaque silver as charge collecting electrodes. *Energy Environ. Sci.* **2015**, *8*, 1690–1697.

[74] Hashmi, S. G.; Ozkan, M.; Halme, J.; Misic, K. D.; Zakeeruddin, S. M.; Paltakari, J.; Grätzel, M.; Lund, P. D. High performance dye-sensitized solar cells with inkjet printed ionic liquid electrolyte. *Nano Energy* **2015**, *17*, 206–215.

[75] Hashmi, S. G.; Özkan, M.; Halme, J.; Zakeeruddin, S. M.; Paltakari, J.; Grätzel, M.; Lund, P. D. Dye-sensitized solar cells with inkjet-printed dyes. *Energy Environ. Sci.* **2016**, *9*, 2453–2462.

[76] Hashmi, S. G.; Martineau, D.; Li, X.; Ozkan, M.; Tiihonen, A.; Dar, M. I.; Sarikka, T.; Zakeeruddin, S. M.; Paltakari, J.; Lund, P. D. et al. Air processed inkjet infiltrated carbon based printed perovskite solar cells with high stability and reproducibility. *Adv. Mater. Technol.* **2017**, *2*, 1600183.

[77] Yang, Z. B.; Chueh, C. C.; Zuo, F.; Kim, J. H.; Liang, P. W.; Jen, A. K. Y. High-performance fully printable perovskite solar cells via blade-coating technique under the ambient condition. *Adv. Energy Mater.* **2015**, *5*, 1500328.

[78] Mei, A. Y.; Li, X.; Liu, L. F.; Ku, Z. L.; Liu, T. F.; Rong, Y. G.; Xu, M.; Hu, M.; Chen, J. Z.; Yang, Y. et al. A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science* **2014**, *345*, 295–298.

[79] Etgar, L.; Gao, P.; Xue, Z. S.; Peng, Q.; Chandiran, A. K.; Liu, B.; Nazeeruddin, M. K.; Grätzel, M. Mesoscopic $CH_3NH_3PbI_3/TiO_2$ heterojunction solar cells. *J. Am. Chem. Soc.* **2012**, *134*, 17396–17399.

[80] Ku, Z. L.; Rong, Y. G.; Xu, M.; Liu, T. F.; Han, H. W. Full printable processed mesoscopic $CH_3NH_3PbI_3/TiO_2$ hetero-junction solar cells with carbon counter electrode. *Sci. Rep.* **2013**, *3*, 3132.

[81] Liu, L. F.; Mei, A. Y.; Liu, T. F.; Jiang, P.; Sheng, Y. S.; Zhang, L. J.; Han, H. W. Fully printable mesoscopic perovskite solar cells with organic silane self-assembled monolayer. *J. Am. Chem. Soc.* **2015**, *137*, 1790–1793.

[82] Xu, M.; Rong, Y. G.; Ku, Z. L.; Mei, A. Y.; Liu, T. F.; Zhang, L. J.; Li, X.; Han, H. W. Highly ordered mesoporous carbon for mesoscopic $CH_3NH_3PbI_3/TiO_2$ heterojunction solar cell. *J. Mater. Chem. A* **2014**, *2*, 8607–8611.

[83] Hu, M.; Liu, L.; Mei, A.; Yang, Y.; Liu, T.; Han, H. Efficient hole-conductor-free, fully printable mesoscopic perovskite solar cells with a broad light harvester $NH_2CH{=}NH_2PbI_3$. *J. Mater. Chem. A* **2014**, *2*, 17115–17121.

[84] Cao, K.; Zuo, Z. X.; Cui, J.; Shen, Y.; Moehl, T.; Zakeeruddin, S. M.; Grätzel, M.; Wang, M. K. Efficient screen printed perovskite solar cells based on mesoscopic $TiO_2/Al_2O_3/NiO$/carbon architecture. *Nano Energy* **2015**, *17*, 171–179.

[85] Chen, J. Z.; Rong, Y. G.; Mei, A. Y.; Xiong, Y. L.; Liu, T. F.; Sheng, Y. S.; Jiang, P.; Hong, L.; Guan, Y. J.; Zhu, X. T. Hole-conductor-free fully printable mesoscopic solar cell with mixed-anion perovskite $CH_3NH_3PbI_{(3-x)}(BF_4)_x$. *Adv. Energy Mater.* **2016**, *6*, 1502009.

[86] Hu, Y.; Si, S.; Mei, A. Y.; Rong, Y. G.; Liu, H. W.; Li, X.; Han, H. W. Stable large-area (10 × 10 cm^2) printable mesoscopic perovskite module exceeding 10% efficiency. *Solar RRL* **2017**, *1*, 1600019.

[87] Minemawari, H.; Yamada, T.; Matsui, H.; Tsutsumi, J.; Haas, S.; Chiba, R.; Kumai, R.; Hasegawa, T. Inkjet printing of single-crystal films. *Nature* **2011**, *475*, 364–367.

[88] Hoth, C. N.; Schilinsky, P.; Choulis, S. A.; Brabec, C. J. Printing highly efficient organic solar cells. *Nano Lett.* **2008**, *8*, 2806–2813.

[89] Yu, Y. L.; Nakano, M.; Ikeda, T. Photomechanics: Directed bending of a polymer film by light. *Nature* **2003**, *425*, 145.

[90] Galassi, C. Processing of porous ceramics: Piezoelectric materials. *J. Eur. Ceram. Soc.* **2006**, *26*, 2951–2958.

[91] Maas, R.; Koch, M.; Harris, N. R.; White, N. M.; Evans, A. G. R. Thick-film printing of PZT onto silicon. *Mater. Lett.* **1997**, *31*, 109–112.

[92] Emamian, S.; Narakathu, B. B.; Chlaihawi, A. A.; Bazuin, B. J.; Atashbar, M. Z. Screen printing of flexible piezoelectric based device on polyethylene terephthalate (PET) and paper for touch and force sensing applications. *Sens. Actuators A: Phys.* **2017**, *263*, 639–647.

[93] Lee, Y.; Kim, W.; Bhatia, D.; Hwang, H. J.; Lee, S.; Choi, D. Cam-based sustainable triboelectric nanogenerators with a resolution-free 3D-printed system. *Nano Energy* **2017**, *38*, 326–334.

[94] Jeerapan, I.; Sempionatto, J. R.; Pavinatto, A.; You, J. M.; Wang, J. Stretchable biofuel cells as wearable textile-based self-powered sensors. *J. Mater. Chem. A* **2016**, *4*, 18342–18353.

[95] Kim, D.; Shin, G.; Kang, Y. J.; Kim, W.; Ha, J. S. Fabrication of a stretchable solid-state micro-supercapacitor array. *ACS Nano* **2013**, *7*, 7975–7982.

[96] Wang, K.; Zou, W. J.; Quan, B. G.; Yu, A. F.; Wu, H. P.; Jiang, P.; Wei, Z. X. An all-solid-state flexible micro-supercapacitor on a chip. *Adv. Energy Mater.* **2011**, *1*, 1068–1072.

[97] El-Kady, M. F.; Kaner, R. B. Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage. *Nat. Commun.* **2013**, *4*, 1475.

[98] Gao, W.; Singh, N.; Song, L.; Liu, Z.; Reddy, A. L. M.; Ci, L.; Vajtai, R.; Zhang, Q.; Wei, B. Q.; Ajayan, P. M. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nat. Nanotechnol.* **2011**, *6*, 496–500.

[99] Simon, P.; Gogotsi, Y. Materials for electrochemical capacitors. *Nat. Mater.* **2008**, *7*, 845–854.

[100] Jayalakshmi, M.; Balasubramanian, K. Simple capacitors to supercapacitors—An overview. *Int. J. Electrochem. Sci.* **2008**, *3*, 1196–1217.

[101] Hu, L. B.; Choi, J. W.; Yang, Y.; Jeong, S.; La Mantia, F.; Cui, L. F.; Cui, Y. Highly conductive paper for energy-storage devices. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 21490–21494.

[102] Jost, K.; Perez, C. R.; McDonough, J. K.; Presser, V.; Heon, M.; Dion, G.; Gogotsi, Y. Carbon coated textiles for flexible energy storage. *Energy Environ. Sci.* **2011**, *4*, 5060–5067.

[103] Le, L. T.; Ervin, M. H.; Qiu, H. W.; Fuchs, B. E.; Lee, W. Y. Graphene supercapacitor electrodes fabricated by inkjet printing and thermal reduction of graphene oxide. *Electrochem. Commun.* **2011**, *13*, 355–358.

[104] Bandodkar, A. J.; López, C. S.; Mohan, A. M. V.; Yin, L.; Kumar, R.; Wang, J. All-printed magnetically self-healing electrochemical devices. *Sci. Adv.* **2016**, *2*, e1601465.

[105] Li, R. Z.; Peng, R.; Kihm, K. D.; Bai, S.; Bridges, D.; Tumuluri, U.; Wu, Z.; Zhang, T.; Compagnini, G.; Feng, Z. et al. High-rate in-plane micro-supercapacitors scribed onto photo paper using *in situ* femtolaser-reduced graphene oxide/Au nanoparticle microelectrodes. *Energy Environ. Sci.* **2016**, *9*, 1458–1467.

[106] Choi, K. H.; Yoo, J.; Lee, C. K.; Lee, S. Y. All-inkjet-printed, solid-state flexible supercapacitors on paper. *Energy Environ. Sci.* **2016**, *9*, 2812–2821.

[107] Cai, J. G.; Lv, C.; Watanabe, A. Cost-effective fabrication of high-performance flexible all-solid-state carbon micro-supercapacitors by blue-violet laser direct writing and further surface treatment. *J. Mater. Chem. A* **2016**, *4*, 1671–1679.

[108] Pang, H.; Zhang, Y. Z.; Lai, W. Y.; Hu, Z.; Huang, W. Lamellar $K_2Co_3(P_2O_7)_2{\cdot}2H_2O$ nanocrystal whiskers: High-performance flexible all-solid-state asymmetric micro-supercapacitors via inkjet printing. *Nano Energy* **2015**, *15*, 303–312.

[109] Li, Y.; Fu, Z. Y.; Su, B. L. Hierarchically structured porous materials for energy conversion and storage. *Adv. Funct. Mater.* **2012**, *22*, 4634–4667.

[110] Li, H.; Tao, Y.; Zheng, X. Y.; Luo, J. Y.; Kang, F. Y.; Cheng, H. M.; Yang, Q. H. Ultra-thick graphene bulk supercapacitor electrodes for compact energy storage. *Energy Environ. Sci.* **2016**, *9*, 3135–3142.

[111] Vu, A.; Qian, Y. Q.; Stein, A. Porous electrode materials for lithium-ion batteries—How to prepare them and what makes them special. *Adv. Energy Mater.* **2012**, *2*, 1056–1085.

[112] Blake, A. J.; Kohlmeyer, R. R.; Hardin, J. O.; Carmona, E. A.; Maruyama, B.; Berrigan, J. D.; Huang, H.; Durstock, M. F. 3D printable ceramic–polymer electrolytes for flexible high-performance Li-ion batteries with enhanced thermal stability. *Adv. Energy Mater.* **2017**, *7*, 1602920.

[113] Ning, H. L.; Pikul, J. H.; Zhang, R. Y.; Li, X. J.; Xu, S.; Wang, J. J.; Rogers, J. A.; King, W. P.; Braun, P. V. Holographic patterning of high-performance on-chip 3D lithium-ion microbatteries. *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 6573–6578.

[114] Zhu, C.; Liu, T. Y.; Qian, F.; Han, T. Y. J.; Duoss, E. B.; Kuntz, J. D.; Spadaccini, C. M.; Worsley, M. A.; Li, Y. Supercapacitors based on three-dimensional hierarchical graphene aerogels with periodic macropores. *Nano Lett.* **2016**, *16*, 3448–3456.

[115] El-Kady, M. F.; Strong, V.; Dubin, S.; Kaner, R. B. Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. *Science* **2012**, *335*, 1326–1330.

[116] Lin, Y. J.; Gao, Y.; Fan, Z. Y. Printable fabrication of nanocoral-structured electrodes for high-performance flexible and planar supercapacitor with artistic design. *Adv. Mater.* **2017**, *29*, 1701736.

[117] Zhao, C.; Wang, C. Y.; Gorkin, R.; Beirne, S.; Shu, K. W.; Wallace, G. G. Three dimensional (3D) printed electrodes for interdigitated supercapacitors. *Electrochem. Commun.* **2014**, *41*, 20–23.

[118] Hu, J. T.; Jiang, Y.; Cui, S. H.; Duan, Y. D.; Liu, T. C.; Guo, H.; Lin, L. P.; Lin, Y.; Zheng, J. X.; Amine, K. et al. 3D-printed cathodes of $LiMn_{1-x}Fe_xPO_4$ nanocrystals achieve both ultrahigh rate and high capacity for advanced lithium -ion battery. *Adv. Energy Mater.* **2016**, *6*, 1600856.

[119] Gaikwad, A. M.; Steingart, D. A.; Nga Ng, T.; Schwartz, D. E.; Whiting, G. L. A flexible high potential printed battery for powering printed electronics. *Appl. Phys. Lett.* **2013**, *102*, 233302.

[120] Braam, K.; Subramanian, V. A stencil printed, high energy density silver oxide battery using a novel photopolymerizable poly(acrylic acid) separator. *Adv. Mater.* **2015**, *27*, 689–694.

[121] Gaikwad, A. M.; Whiting, G. L.; Steingart, D. A.; Arias,

A. C. Highly flexible, printed alkaline batteries based on mesh-embedded electrodes. *Adv. Mater.* **2011**, *23*, 3251–3255.

[122] Kumar, R.; Shin, J.; Yin, L.; You, J. M.; Meng, Y. S.; Wang, J. All-printed, stretchable Zn-Ag_2O rechargeable battery via hyperelastic binder for self-powering wearable electronics. *Adv. Energy Mater.* **2017**, *7*, 1602096.

[123] Fu, K.; Wang, Y. B.; Yan, C. Y.; Yao, Y. G.; Chen, Y.; Dai, J. Q.; Lacey, S.; Wang, Y. B.; Wan, J. Y.; Li, T. et al. Graphene oxide-based electrode inks for 3D-printed lithium-ion batteries. *Adv. Mater.* **2016**, *28*, 2587–2594.

[124] Milroy, C. A.; Jang, S.; Fujimori, T.; Dodabalapur, A.; Manthiram, A. Inkjet-printed lithium–sulfur microcathodes for all-printed, integrated nanomanufacturing. *Small* **2017**, *13*, 1603786.

[125] Kim, S. H.; Choi, K. H.; Cho, S. J.; Choi, S.; Park, S.; Lee, S. Y. Printable solid-state lithium-ion batteries: A new route toward shape-conformable power sources with aesthetic versatility for flexible electronics. *Nano Lett.* **2015**, *15*, 5168–5177.

[126] Kim, S. H.; Choi, K. H.; Cho, S. J.; Yoo, J.; Lee, S. S.; Lee, S. Y. Flexible/shape-versatile, bipolar all-solid-state lithium-ion batteries prepared by multistage printing. *Energy Enviro. Sci.* **2018**, *11*, 321–330.

[127] Gao, Z.; Bumgardner, C.; Song, N.; Zhang, Y.; Li, J.; Li, X. Cotton-textile-enabled flexible self-sustaining power packs via roll-to-roll fabrication. *Nat. Commun.* **2016**, *7*, 11586.

[128] Mahmoudzadeh, M. A.; Usgaocar, A. R.; Giorgio, J.; Officer, D. L.; Wallace, G. G.; Madden, J. D. A high energy density solar rechargeable redox battery. *J. Mater. Chem. A* **2016**, *4*, 3446–3452.

[129] Guo, W. X.; Xue, X. Y.; Wang, S. H.; Lin, C. J.; Wang, Z. L. An integrated power pack of dye-sensitized solar cell and Li battery based on double-sided TiO_2 nanotube arrays. *Nano Lett.* **2012**, *12*, 2520–2523.

[130] Chen, X. L.; Sun, H.; Yang, Z. B.; Guan, G. Z.; Zhang, Z. T.; Qiu, L. B.; Peng, H. S. A novel "energy fiber" by coaxially integrating dye-sensitized solar cell and electrochemical capacitor. *J. Mater. Chem. A* **2014**, *2*, 1897–1902.

[131] Xu, X. B.; Li, S. H.; Zhang, H.; Shen, Y.; Zakeeruddin, S. M.; Graetzel, M.; Cheng, Y. B.; Wang, M. K. A power pack based on organometallic perovskite solar cell and supercapacitor. *ACS Nano* **2015**, *9*, 1782–1787.

[132] Cohn, A. P.; Erwin, W. R.; Share, K.; Oakes, L.; Westover, A. S.; Carter, R. E.; Bardhan, R.; Pint, C. L. All silicon electrode photocapacitor for integrated energy storage and conversion. *Nano Lett.* **2015**, *15*, 2727–2731.

[133] Bae, J.; Park, Y. J.; Lee, M.; Cha, S. N.; Choi, Y. J.; Lee, C. S.; Kim, J. M.; Wang, Z. L. Single-fiber-based hybridization of energy converters and storage units using graphene as electrodes. *Adv. Mater.* **2011**, *23*, 3446–3449.

[134] Schmidt, D.; Hager, M. D.; Schubert, U. S. Photo-rechargeable electric energy storage systems. *Adv. Energy Mater.* **2016**, *6*, 1500369.

[135] Xu, J. T.; Chen, Y. H.; Dai, L. M. Efficiently photo-charging lithium-ion battery by perovskite solar cell. *Nat. Commun.* **2015**, *6*, 8103.

[136] Zhou, F. C.; Ren, Z. W.; Zhao, Y. D.; Shen, X. P.; Wang, A. W.; Li, Y. Y.; Surya, C.; Chai, Y. Perovskite photovoltachromic supercapacitor with all-transparent electrodes. *ACS Nano* **2016**, *10*, 5900–5908.

[137] Shi, C. L.; Dong, H.; Zhu, R.; Li, H.; Sun, Y. C.; Xu, D. S.; Zhao, Q.; Yu, D. P. An "all-in-one" mesh-typed integrated energy unit for both photoelectric conversion and energy storage in uniform electrochemical system. *Nano Energy* **2015**, *13*, 670–678.

[138] Yang, Z. B.; Li, L.; Luo, Y. F.; He, R. X.; Qiu, L. B.; Lin, H. J.; Peng, H. S. An integrated device for both photoelectric conversion and energy storage based on free-standing and aligned carbon nanotube film. *J. Mater. Chem. A* **2013**, *1*, 954–958.

[139] Chen, T.; Qiu, L. B.; Yang, Z. B.; Cai, Z. B.; Ren, J.; Li, H. P.; Lin, H. J.; Sun, X. M.; Peng, H. S. An integrated "energy wire" for both photoelectric conversion and energy storage. *Angew. Chem., Int. Ed.* **2012**, *51*, 11977–11980.

[140] Zhang, Z. T.; Chen, X. L.; Chen, P. N.; Guan, G. Z.; Qiu, L. B.; Lin, H. J.; Yang, Z. B.; Bai, W. Y.; Luo, Y. F.; Peng, H. S. Integrated polymer solar cell and electrochemical supercapacitor in a flexible and stable fiber format. *Adv. Mater.* **2014**, *26*, 466–470.

[141] Fu, Y. P.; Wu, H. W.; Ye, S. Y.; Cai, X.; Yu, X.; Hou, S. C.; Kafafy, H.; Zou, D. C. Integrated power fiber for energy conversion and storage. *Energy Environ. Sci.* **2013**, *6*, 805–812.

[142] Xia, X. H.; Ku, Z. L.; Zhou, D.; Zhong, Y.; Zhang, Y. Q.; Wang, Y. D.; Huang, M. J.; Tu, J. P.; Fan, H. J. Perovskite solar cell powered electrochromic batteries for smart windows. *Mater. Horiz.* **2016**, *3*, 588–595.

[143] Cai, G. F.; Darmawan, P.; Cui, M. Q.; Chen, J. W.; Wang, X.; Eh, A. L. S.; Magdassi, S.; Lee, P. S. Inkjet-printed all solid-state electrochromic devices based on NiO/WO_3 nanoparticle complementary electrodes. *Nanoscale* **2016**, *8*, 348–357.

[144] Berggren, M.; Nilsson, D.; Robinson, N. D. Organic materials for printed electronics. *Nat. Mater.* **2007**, *6*, 3–5.