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Direct Laser Writing of Supercapacitors

Litty V. Thekkekara

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Abstract

Direct laser writing is a single-step fabrication technique for the micro and nanostructures even below the sub-diffraction limits. In recent times, the technique is adapted to the fabrication of on-chip energy storages with additional features of flexibility and stretchability. The major category of the energy storages taken into consideration for laser writing belongs to the family of supercapacitors which is known for the high rate of charge transfer, longer life spans and lesser charging times in comparison with traditional batteries. The technology explores the possibilities of non-explosive all solid-state energy storage integration with portable and wearable applications. These features can enable the development of self-powered autonomous devices, vehicles and self-reliant infrastructures. In this chapter, we discuss the progress, challenges and perspectives of micro-supercapacitors fabricated using direct laser writing.

Keywords: direct laser writing, nanomaterials, on-chip supercapacitors, flexible

1. Introduction

The rapid technological advancements in this era demand the provision of electricity for the maintenance. In addition, the household requirements for the electricity are also in its peak of demand. The current energy resources like coal and oil are irreversible and depleting at a faster rate. On the other hand, the developments of renewable energy resources like solar and wind energies are limited by the intermittent nature and it demands the provision of energy storages to be accompanied which leads to the high cost of the resulting commercial energy modules resulting in a less attractiveness in the market. In addition, the disposal issues generated by the energy storages like traditional batteries are a major concern for the environment. On the other hand, green on-chip energy storages offer an efficient, cost-effective platform for integrated miniaturized devices, energy-harvesting, self-reliant residential and commercial buildings.

Micro-supercapacitors (MSCs) are a recent addition to the environmentally friendly energy storages with higher charge-discharge transfer rates on the contrary to traditional batteries [1]. The batteries whose lifetime is restricted due to the involvement of electrochemical redox reaction create the issues of additional storage and disposal space where MSCs which can be fabricated on any substrates utilize the electrostatic interactions of electrode-electrolyte materials.

The performance of MSC is determined by the available active electrode material and the voltage window of the electrolyte [2]. Based on the electrode-electrolyte interactions, the supercapacitors are divided into three major types: (i) electrochemical double layer capacitor (EDLC), (ii) pseudocapacitors and (iii) hybrid supercapacitors. EDLC works based on the electrostatic interaction between electrode and electrolyte ions where pseudocapacitors involve the redox reaction between electrodes and electrolyte ions similar to the batteries. A strong pseudo-capacitance is not desirable in many applications due to the slow response time and high capacitance decay rate [3]. Hybrid supercapacitors combine the EDLC and pseudocapacitance effects in the performance which can be used to compensate the drawbacks of current commercial supercapacitors to become a replacement for the batteries.

Several methods are used for the fabrication of various kind of supercapacitors. The main categories are chemical techniques based on the nanomaterials [4] and electron beam lithography (EBL) [5]. The lesser integrability for flexible applications and cost involved in the fabrication of these techniques make them less desirable for industrial scale production of commercial applications. The recent reports on the use of direct laser writing (DLW) technique for the supercapacitor fabrication [6] is a fast and reliable single-step method with the possible integration of all substrates.

2. Direct laser writing

The DLW method mainly uses an ultrafast laser (femtosecond, fs or picosecond, ps lasers) [7] but recently continuous wave (cw) lasers are also used for specific materials [8]. The laser
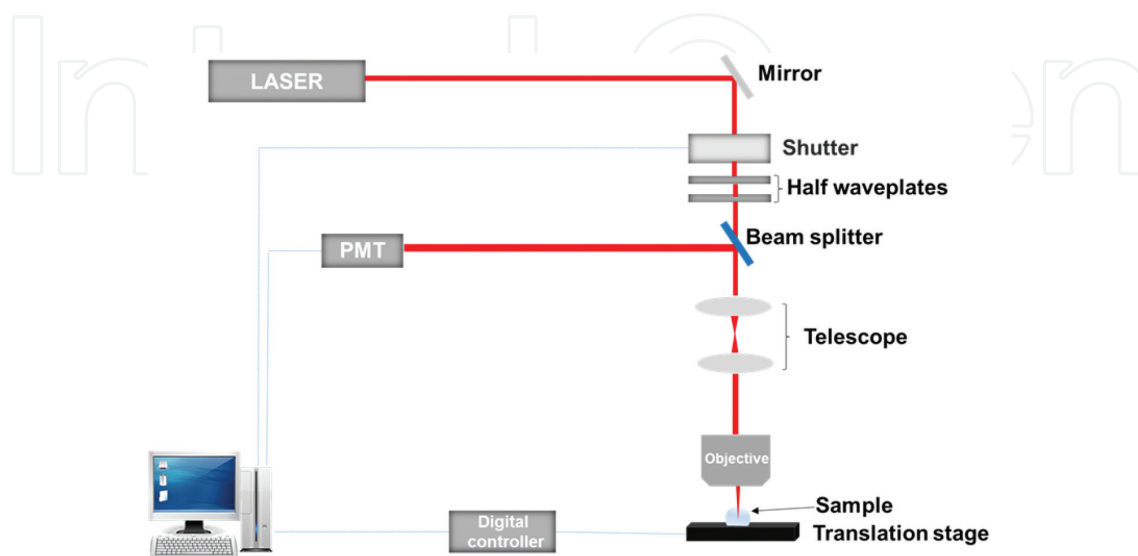
Figure 1. Schematic of direct laser writing setup.

source is tightly focused to a diffraction limited focal spot, using an objective made of different numerical apertures (NAs) forming a high intensity of laser beam. The transparency at the wavelength and spot size uniformity of the used laser beam as well as the sample uniformity is highly necessary to obtain good quality structures. However, due to the high-intensity generation from the tight focusing conditions, the non-linear process is triggered at the focal spot, which can lead to the photo-polymerization [9], microexplosion [10], photoreduction [11] and micro-machining process [12] in the material leaving remaining area unmodified. The sample moves with the help of three-dimensional (3D) translation stage according to the pre-programmed pattern design. The schematic of the DLW setup is given in **Figure 1**.

3. Direct laser writing of micro-supercapacitors

In the following sections, a detailed understanding of the DLW process on various electrode materials for MSCs is discussed.

3.1. Electrode materials

The electrodes of MSC require high active surface area, long-term stability, resistance to electrochemical oxidation or reduction, the capability of multiple cycling materials, optimum pore size distribution, minimized ohmic resistance with the contacts, sufficient electrode-electrolyte solution contact interface, mechanical integrity and less self-discharge [1].

3.1.1. Laser-scribed graphene and its derivatives

Materials such as carbon and its derivatives like porous activated carbon, carbon nanotubes, carbon aerogels or carbon-metal composites have a higher surface area of 100–220 m^2 g^{-1} and they exhibit excellent stability but limited capacitance [4]. For activated carbons, only about 10–20% of the theoretical capacitance can be achieved due to the micropores that are inaccessible by the electrolyte [13]. The carbon nanotubes do not exhibit satisfactory capacitance unless a conducting polymer [14] is used to form a pseudocapacitance.

Graphene is a form of carbon with the high surface area up to 2675 m^2/g and the intrinsic capacitance of 21 $\mu F/cm^2$, which sets the upper limit of EDLC capacitance of all carbon-based materials [15]. In addition, both faces of graphene sheets are readily accessible by the electrolyte. However, in practical applications, the surface area of graphene will be much reduced due to agglomeration.

Laser-scribed graphene (LSG), obtained from the DLW in graphene oxide (GO) material, is a cost-effective tunable alternative to graphene. The LSG films are used to fabricate MSC and other integrable applications and first reported from Ajayan's group with the use of carbon dioxide (CO_2) laser beam by adopting the design concept from capacitors [6] in 2011. This work is followed by the Kaner's group in 2012 through the production of high-performance LSG sandwich energy storages using a DVD burner [16].

Furthermore, two famous works came in the following years: The first work demonstrates the fabrication of all solid state MSCs using ionic gel electrolyte with interdigitated electrodes.

This kind of electrodes improves electrolyte ion transport that effectively improves the energy storage density and power density up to 10^{-3} Wh/cm^3 and 10^1 W/cm^3 (**Figure 2**) [17]. The next reported energy storage used the pre-patterned CO_2 laser irradiation on polyethylene terephthalate (PET) substrate to generate the high-quality graphene for the energy storage [18].

3.1.2. Oxides and polymers

The DLW method can be used for the fabrication of pseudocapacitors using different materials like ruthenium oxide (RuO_2) and manganese dioxide (MnO_2) and conductive polymers like polyaniline (PANI) with the LSG material becomes a direction of interest to achieve the high-performance MSCs in the given area [19]. For example, the hybrid of ultrathin MSCs made of MnO_2 sheets and graphene sheets using DLW offers an electrochemically active surface for fast absorption/desorption of electrolyte ions [20]. The contributions of additional interfaces at the hybridized interlayer areas to accelerate charge transport during charge/discharge process result in an energy density and power density of 2.4 mWh/cm^3 and 298 mW/cm^3, respectively.
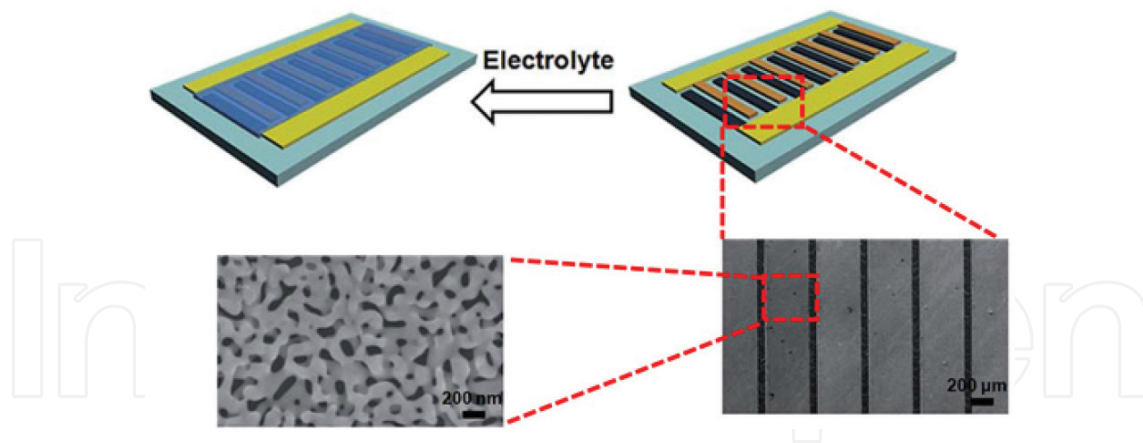
3.1.3. Porous gold

The recent development of the well-connected nanoporous gold film using DLW is used in the fabrication of interdigital electrode materials for MSCs with high mechanical flexibility [21]. These MSCs exhibit a capacitance of 127 F cm^{-3} and energy density of 0.045 Wh cm^{-3}. The gold metal is known for its high electrical conductivity and the concept adopted can be used efficiently to integrate with devices in lesser areal footprints (**Figure 3**).

The high-performance integrable MSCs fabricated using DLW which can be integrated with all platforms can be the future of energy storages.
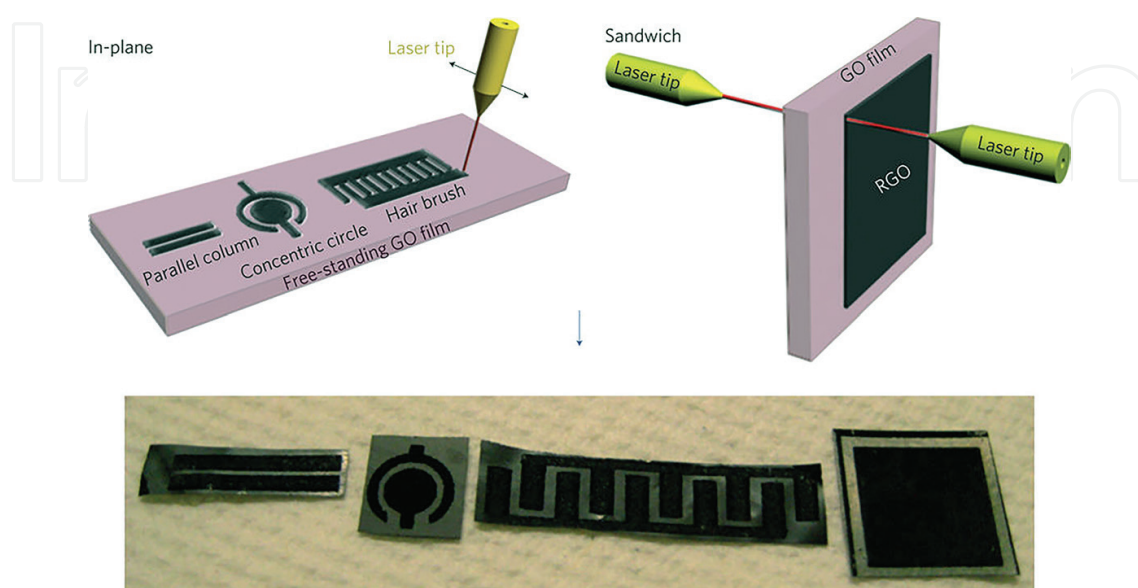
Figure 2. Direct laser writing of MSC. Reproduced with permission [6]. Copyright 2011, Nature Publishing Group.

Figure 3. Direct laser writing for the fabrication of nanoporous gold film electrodes coated with MnO_2 [21]. Copyright 2016, Royal Society of Chemistry.

3.2. Matrix-assisted pulsed laser evaporation direct write (MAPLE-DW)

MAPLE-DW involves the laser forwarded transfer of liquid transfer matrix (transfer vehicle), which is composed of material to be deposited on the substrate below. A relatively flat and uniform film is achieved with the presence of liquid without the need for high temperature or post-processing involved in the lithographic techniques [22]. Pseudocapacitors from $RuO_2 \cdot 0.5$ H_2O with the sulfuric acid as transfer vehicle result in an ideal capacitor behavior instead of the contamination generated from the transfer vehicles [23]. Moreover, the obtained specific (volumetric) capacitance of 720 F/g is comparable to the other laser-printed MSCs (**Figure 4**).

3.3. Parameter calculation

Generally, DLW-MSC performance is calculated in specific (volumetric) and areal capacitance in metric quantity rather than the mass of the obtained electrodes due to the presence of significantly low volumes.

In brief, the specific capacitance was calculated from galvanostatic (CC) curves at different current densities by the formula:
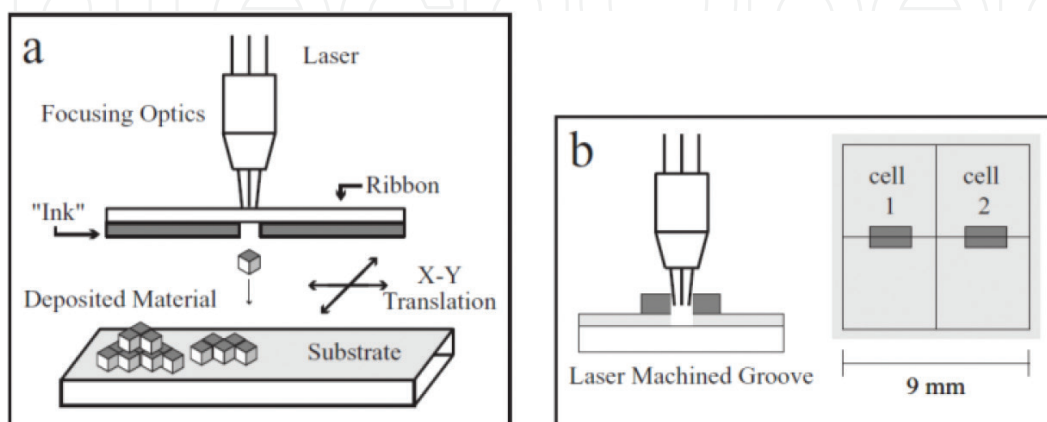
Figure 4. MAPLE-DW method for the fabrication of MSC. (a) Schematic of MAPLE-DW apparatus showing the method of forward laser transfer of an "ink" layer (b) Sample geometry: the two pseudocapacitors cells are 1 mm × 2 mm × 10 μm prior to laser machining [23]. Copyright 2002, SPIE Publishing Group.

$$C_{device=} i/\{-dV/dt\} \tag{1}$$

where i is the applied current (in amps, A) and dV/dt is the slope of the discharge curve (in volts per second, V/s).

Volumetric capacitance was given by

$$C_{vol} = C_{device}/V \tag{2}$$

where A and V refer to the area (cm^2) and volume (cm^3), respectively.

The power density of the device is calculated from galvanostatic curves at different charge/discharge densities and given by the formula:

$$P = (\Delta E)^2/4\,R_{ESR}\,V \tag{3}$$

where P is the power in W/cm^3, ΔE is the operating voltage window and R_{ESR} is the internal resistance of the device and can be given by the formula:

The energy density of the device can be calculated by the formula:

$$E = Cv^* (\Delta E)^2/(2^* 3600) \tag{4}$$

where E is the energy density in Wh/cm^3, Cv is the volumetric capacitance and ΔE is the operating voltage window, V.

4. Challenges and perspectives

4.1. Electrode designs

The current energy storage devices are usually too heavy, rigid and bulky to match the requirements of flexible electronics [1]. Therefore, there is keen interest in the development of the light, elastic and mechanical properties with shape conformability in the next generation of energy storages. However, the bottleneck issues faced by the current MSCs are the lesser surface area of the electrode material and the more substantial mean ionic path of the electrolyte ions due to the diffraction-limited spatial resolution of the laser beam used for the preparation of electrode materials [24].

The first generation of MSCs is mainly involved in the 2D planar designs. However, these planar 2D electrodes are limited in the amount of energy storage capacities; on the other hand, increasing the thickness of the electrodes results in the low transportation of the electrolyte ions, which limits the rate transfer capabilities. The issue is initially addressed by Gao et al. where a variety of on-chip designs are tested to obtain an optimized design concept for the self-powering on-chip applications, and the interdigital electrode designs seem to be out-performing the other designs [6].

However, the fast growth of technologies like the flexible MEMS or self-reliant buildings demands the high-performance on-chip energy storages.

4.1.1. Fractal designs

New electrode designs can be a possible solution to improve the energy density of MSCs, and an example is the origami designs utilized in the flexible energy storages and electronics [25]. In the case of integrable energy storages using DLW, a better choice can be biomimetic designs [26]. The *Fern Leafs* is an efficient platform for energy storage in biological processes such as photosynthesis enabled by water transport on its vein density [27] as well as information compression [28]. The biomimetic structures inspired by the internal structure of *American Fern* (*Polystichum munitum*), which is also known as the *Barnsley fractals* [29], are a possible design for the enhancement of the active electrode material loading per unit area using DLW [30]. American fern leafs with self-repeating patterns of internal structure resemble the fractal design family known as *space-filling curves* [31].

From the comparison between the various designs of the space-filling fractal family, it is found that the Hilbert space-filling designs have the highest active surface area comparing to the other designs. The resulting MSCs have an energy density of 10^{-1} Whcm^{-3} without compensating the rate of charge transfer (power density) and have a flexibility up to 60° [30]. The fractal designs offer a further chance to improve the performance of MSCs and still need a detailed investigation of various fractal families (**Figure 5**).

4.1.2. Three-dimensional micro-supercapacitors

Printing of high-performance MSCs in lesser footprints is possible with the development of three-dimensional (3D) MSCs. In 2015, Tour's group demonstrated the concept of the layer by layer stacking of individual laser-induced graphene (LIG) MSCs obtained from the PET sheets, which result in an areal capacitance of >9 mF/cm^2 as shown in **Figure 6** [32] and can be considered for the ultra-portable and flexible application levels. In addition, reports of using multilayer structures made of rGO/Au particles [33] and LIG from polyamides using femto-second laser reduction with improved spatial resolution are promising directions for the 3D energy storages [34] (**Table 1**).
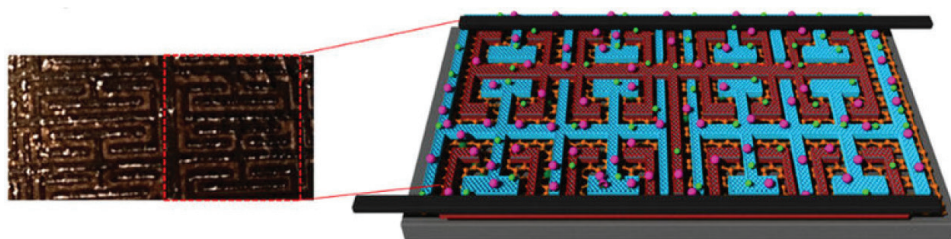
Figure 5. Fractal MSC [30]. Copyright 2017, Nature Publishing Group.
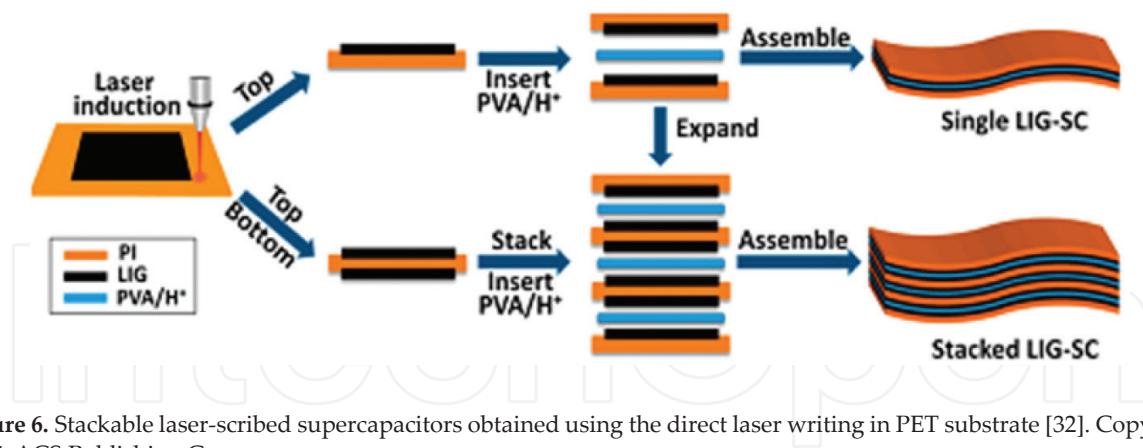
Figure 6. Stackable laser-scribed supercapacitors obtained using the direct laser writing in PET substrate [32]. Copyright 2015, ACS Publishing Group.

	Material	Methods	Properties
Ajayan [6]	Hydrated graphene oxide films	Direct laser writing (cw)	Specific capacitance of 5 mF/cm² in water
Kaner [16]	Graphene oxide	Direct laser writing (cw)	Energy density- 10^{-2} Whcm^{-3}
Kaner [17]	Graphene oxide	Direct laser writing (cw)	Power density of 200 W cm^{-3} at 10,000 cycles in PVA-sulfuric acid
Tour [18]	Polymer	Direct laser writing (µs)	BMIM-BF$_4$ electrolyte with a specific capacitance of >4 mF cm^{-2} and power densities ~ 9 mWcm^{-2}
Hu [33]	Graphene oxide/gold nanoparticle	Direct laser writing (fs)	PVA/ H2SO4 electrolyte with specific capacitance of 0.77 mFcm^{-2}
Gu [30]	Graphene oxide	Direct laser writing (cw)	with specific capacitance of 350 mFcm^{-2}
Hu [34]	Multilayer polymer	Direct laser writing (fs)	With a specific capacitance of 42 mFcm^{-2}

Table 1. Summary of the graphene supercapacitors fabricated using direct laser writing.

5. Electrolytes

The electrolyte has a significant role in determining other essential properties such as the energy density, power density, internal resistance, rate performance, operating temperature range, cycling lifetime, self-discharge, non-volatile nature and toxicity of the energy storage. The electrochemical range of an electrolyte decides the cell voltage window of the energy storages like the batteries and supercapacitors [9] as shown in the equation,

$$E = 1/2 \, CV \tag{5}$$

where E is the energy density, C is the specific capacitance and V is the cell voltage.

So far, the electrolytes used in an energy storage can be classified as liquid electrolytes and solid/quasi-solid state electrolytes [35]. Liquid electrolytes can be further grouped as aqueous electrolytes with a voltage range of 1.0–1.3 V, organic electrolytes within the voltage range of

1–2 V and ionic liquids (ILs) with a voltage range of 3.5–4.0 V. The solid or quasi-solid state electrolytes can be classified as organic and inorganic electrolytes with a voltage range of 2.5–2.7 V.

Among different electrolytes, aqueous ones possess high conductivity and capacitance but are limited by low cell voltage window, whereas organic and IL electrolytes can operate at higher cell voltage windows [36]. ILs are widely used in the energy storages owing to their attractive properties like the non-flammability, low vapor pressure and large operating potential window. Solid state electrolytes are devoid of leakage issues but are limited by the low conductivity.

6. Scale-up process of micro-supercapacitors

The considerable advantage of the DLW-MSC is the possibility of large-scale production with the industrial grade. However, the scale-up process might introduce the difficulties of heat, enhancement of effective series resistance (ESR) and overcharge [1]. In addition, the cost of the process needs to be compatible to the existing battery technology. DLW technique due to its straight single-step process, which combines with the efficient tuning of nanomaterials, can provide an efficient solution to the issue in long term. The successful generation of high-performance MSCs will enable a step closer to the biocompatible light-weight portable and wearable devices as well as the replacement of large area spaces required for the energy storages.

7. Integration with applications

The self-powered autonomous systems will be the future direction with impact in large areas of technologies by the inclusion of additional features like portability, flexibility and stretchability. One of the integrated DLW-MSC with existing renewable technology is discussed below.

7.1. Solar energy storages

Self-powered electronics and buildings, which utilize the renewable energy resources like solar energy, provide a green platform for the next-generation technology and find applications in skyscrapers, flexible, wearable, consumable and portable devices [37]. The primary issue faced by the renewable energies to be considered as the major electricity source such as the intermittent nature which limits the use of those energies during certain climatic conditions or in the remote areas which are isolated from the grid line electricity [38]. The current solar modules used to be accompanied by the energy storages in the commercial market are the traditional batteries, which intake almost 30% of the total cost of the solar module. In addition, the protective storage space for the energy storages becomes a significant issue when it comes to large-scale applications.

An integrated on-chip solar energy storages, which can be simultaneously charged using the solar electricity, can be a possible solution for the problem and energy stored can be used during the required times irrespective of the intermittent solar energy. However, the primary challenge for the integrated solar energy storage is to design the cell structure by incorporating both photoelectric and storage functions. The initial efforts are oriented around co-operating
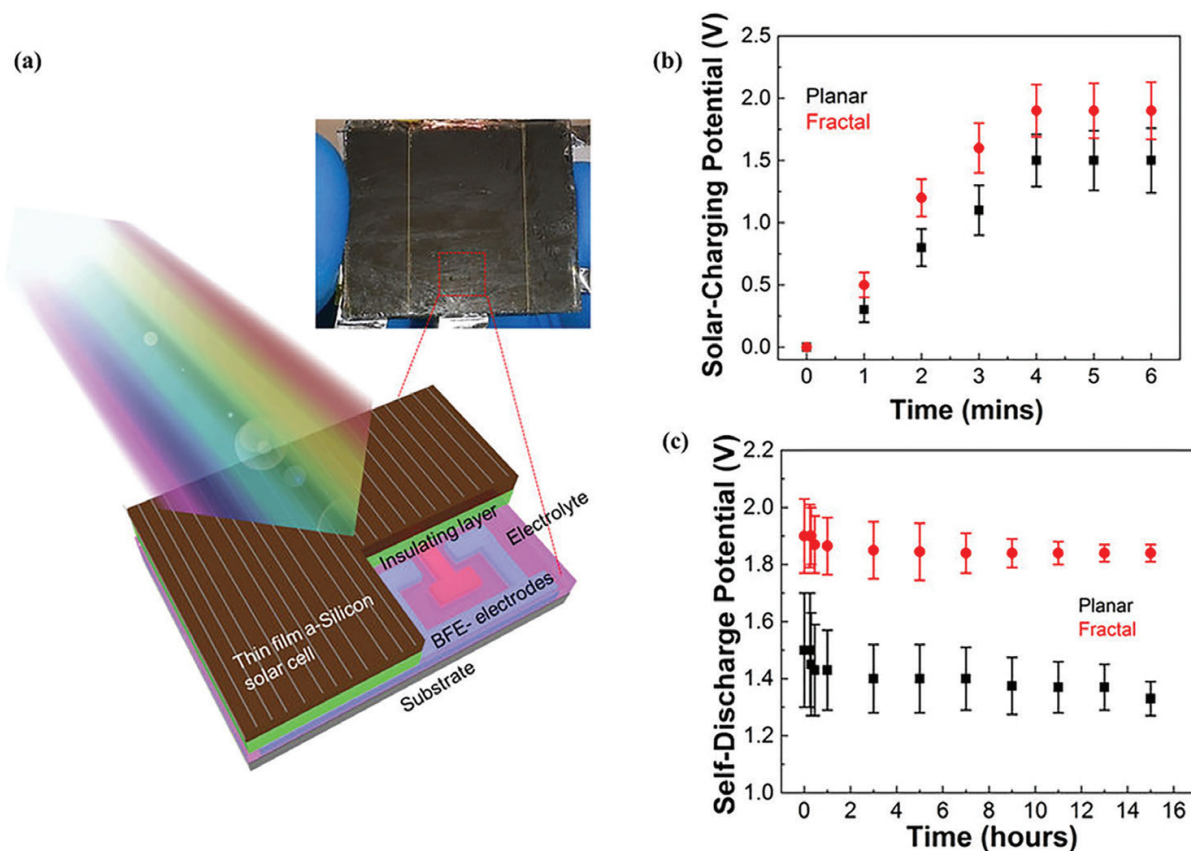
Figure 7. Solar energy storages using fractal electrodes on the reverse side of thin-film silicon solar cells [30]. Copyright 2017, Nature Publishing Group.

both photoelectric and storage functions in a single cell structure [39]. Due to the repeated oxidations and reductions shorten the lifetime of these batteries [1] and chemical storage functions in a single cell structure. The repeated oxidations and reductions shorten the lifetime of these batteries. The energy storages with storage mechanism free from electrochemical reactions as in batteries like capacitors can be a competent way of overcoming the problem.

In order to solve the issues, we developed solar energy storages using LSG electrodes in the interdigital form [40] as well as the fractal electrode designs (**Figure 7**) [30] and integrated on the reverse side of the silicon solar cells. The performance of the obtained solar energy storages is influenced by the efficiency of the solar cells and the discharge time for the output voltage is up to 22 days with excellent charge-discharge cycles of around 800.

8. Conclusions and future trends

Laser beam-material interactions induce the controlled changes in the physical and chemical properties of the electrode materials for MSCs. In addition, the smaller spatial resolution obtained using the tightly controlled focus spot can lead to the enhancement of specific volume load per unit area resulting in efficient storage of electrolyte ions within the layers of the electrodes. The desired electrode patterns fabricated using the writing process enable the supercapacitor features to be included in any substrates with the proper choice of electrolytes.

The improvement of further energy density obtained in laser-scribed supercapacitors using advanced techniques like super-resolution fabrication [41] along with the implementation of multifocal parallel array fabrication [42] can offer the fabrication in short period of time and deployment of self-powered autonomous systems in the next-generation technology like buildings, sensors, imaging, etc.

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Conflict of interest

The author declares no conflict of interest.

Nomenclature

DLW	Direct laser writing
MSC	Micro-supercapacitors
fs	Femtosecond
ps	Picosecond
cw	Continuous wave
NA	Numerical aperture
EDLC	Electrochemical double layer capacitance

Author details

Litty V. Thekkekara

Address all correspondence to: littvarghese.thekkekara@rmit.edu.au

School of Science, RMIT University, Melbourne, Australia

References

[1] Conway BE. Electrochemical supercapacitors: Scientific fundamentals and technological applications. Springer Science & Business Media. 2013. DOI: 10.1007/978-1-4757-3058-6

[2]   Winter M, Brod RJ. What are batteries, fuel cells, and supercapacitors? Chemical Reviews. 2004;**104**(10):4245-4270. DOI: 10.1021/cr020730k

[3]   Conway BE. Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage. Journal of the Electrochemical Society. 1991;**138**(6):1539-1548. DOI: 10.1149/1.2085829

[4]   Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical supercapacitors. Chemical Society Reviews. 2012;**41**(2):797-828. DOI: 10.1039/C1CS15060J

[5]   Lobo DE, Banerjee PC, Easton CD, Majumder M. Miniaturized supercapacitors: Focused ion beam reduced graphene oxide supercapacitors with enhanced performance metrics. Advanced Energy Materials. 2015;**5**(19). DOI: 10.1002/aenm.201500665

[6]   Gao W, Singh N, Song L, Liu Z, Reddy ALM, Ci L, Vajtai R, Zhang Q, Wei B, Ajayan PM. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. Nature Nanotechnology. 2011;**6**(8):496-500. DOI: 10.1038/nnano.2011.110

[7]   Gamaly EG. Femtosecond Laser-Matter Interaction: Theory, Experiments, and Applications. Singapore: CRC Press; 2011

[8]   Do MT, Nguyen TTN, Li Q, Benisty H, Ledoux-Rak I, Lai ND. Submicrometer 3D structures fabrication enabled by one-photon absorption direct laser writing. Optics Express. 2013;**21**(18):20964-20973. DOI: 10.1364/OE.21.020964

[9]   Liska R, Ovsianikov A. Multiphoton Lithography: Techniques, Materials, and Applications. Weinheim: John Wiley & Sons, 2016

[10] Misawa H, Juodkazis S. 3D Laser Microfabrication: Principles and Applications. Weinheim: John Wiley & Sons; 2006

[11] Zhang YL, Guo L, Xia H, Chen QD, Feng J, Sun HB. Photoreduction of graphene oxides: Methods, properties, and applications. Advanced Optical Materials. 2014;**2**(1):10-28. DOI: 10.1002/adom.201300317

[12] Sugioka K, Cheng Y. Ultrafast Laser Processing: From Micro-to Nanoscale. Florida: CRC Press, 2013

[13] Frackowiak E. Carbon materials for supercapacitor application. Physical Chemistry Chemical Physics. 2007;**9**(15):1774-1785. DOI: 10.1039/B618139M

[14] Obreja VV. On the performance of supercapacitors with electrodes based on carbon nanotubes and carbon activated material—A review. Physica E: Low-dimensional Systems and Nanostructures. 2008;**40**(7):2596-2605. DOI: 10.1016/j.physe.2007.09.044

[15] Wang Y, Shi Z, Huang Y, Ma Y, Wang C, Chen M, Chen,Y. Supercapacitor devices based on graphene materials. The Journal of Physical Chemistry C. 2009;**113**(30):13103-13107. DOI: 10.1021/jp902214f

[16] El-Kady MF, Strong V, Dubin S, Kaner RB. Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. Science. 2012;**335**(6074):1326-1330. DOI: 10.1126/science.1216744

[17] El-Kady MF, Kaner RB. Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage. Nature Communications. 2013;**4**:1475. DOI: 10.1038/ncomms2446

[18] Lin J, Peng Z, Liu Y, Ruiz-Zepeda F, Ye R, Samuel EL, Yacaman MJ, Yakobson BI, Tour JM. Laser-induced porous graphene films from commercial polymers. Nature Communications. 2014;**5**:5714. DOI: 10.1038/ncomms6714

[19] Hwang JY, El-Kady MF, Wang Y, Wang L, Shao Y, Marsh K, Ko JM, Kaner RB. 2015. Direct preparation and processing of graphene/RuO_2 nanocomposite electrodes for high-performance capacitive energy storage. Nano Energy. 2015;**18**:57-70. DOI: 10.1016/j.nanoen.2015.09.009

[20] Li L, Zhang J, Peng Z, Li Y, Gao C, Ji Y, Ye R, Kim ND, Zhong Q, Yang Y, Fei H. High-performance Pseudocapacitive Microsupercapacitors from laser-induced Graphene. Advanced Materials. 2016;**28**(5):838-845. DOI: 10.1002/adma.201503333

[21] Zhang C, Xiao J, Qian L, Yuan S, Wang S, Lei P. Planar integration of flexible micro-supercapacitors with ultrafast charge and discharge based on interdigital nanoporous gold electrodes on a chip. Journal of Materials Chemistry A. 2016;**4**(24):9502-9510. DOI: 10.1039/C6TA02219G

[22] Morales M, Munoz-Martin D, Marquez A, Lauzurica S and Molpeceres C. Laser-Induced Forward Transfer Techniques, and Applications. Advances in Laser Materials Processing (Second Edition), pp. 339-379, 2018. ISBN: 978-0-08-101252-9

[23] Arnold C, Wartena R, Pratap B, Swider-Lyons K, Piqué A. Laser direct writing of hydrous ruthenium dioxide micro-Pseudocapacitors. MRS Proceedings. 2001;**698**. DOI: 10.1557/PROC-698-Q3.2.1

[24] Stoller MD, Ruoff RS. Best practice methods for determining an electrode material's performance for ultracapacitors. Energy & Environmental Science. 2010;**3**:1294-1301. DOI: 10.1039/C0EE00074D

[25] Nam I, Kim GP, Park S, Han JW, Yi J. All-solid-state, origami-type foldable supercapacitor chips with integrated series circuit analogues. Energy & Environmental Science. 2014;**7**(3):1095-1102. DOI: 10.1039/c3ee43175d

[26] Bar-Cohen Y. Biomimetics—Using nature to inspire human innovation. Bioinspiration & Biomimetics. 2006;**1**(1):P1. DOI: 10.1088/1748-3182/1/1/P01

[27] Zhang S-B, Sun M, Cao K-F, Hu H, Zhang J-L. Leaf photosynthetic rate of tropical ferns is evolutionarily linked to water transport capacity. PLoS One. 2014;**9**(1):e84682. DOI: 10.1371/J. Pone.0084682.t001

[28] Barnsley MF, Hurd LP. Fractal image compression. A. K. Peters. Ltd; 1993

[29] Barnsley MF. Fractal everywhere. Morgan Kaufmann Publications (1993)

[30] Thekkekara LV, Gu M. Bioinspired fractal electrodes for solar energy storages. Scientific Reports. 2017;**7**:45585. DOI: 10.1038/srep45585

[31] Jordan C. Cours d'analyse. pp. 587-594, Gauthier-Villars, Imprimeur-Libraire (1887)

[32] Peng Z, Lin J, Ye R, Samuel EL, Tour JM. Flexible and stackable laser-induced graphene supercapacitors. ACS Applied Materials & Interfaces. 2015;**7**(5):3414-3419. DOI: 10.1021/am509065d

[33] Li RZ, Peng R, Kihm KD, Bai S, Bridges D, Tumuluri U, Wu Z, Zhang T, Compagnini G, Feng Z and Hu A. 2016. High-rate in-plane micro-supercapacitors scribed onto photo paper using in situ femtolaser-reduced graphene oxide/Au nanoparticle microelectrodes. Energy & Environmental Science. 2016;**9**(4):1458-1467. DOI: 10.1039/C5EE03637B

[34] Wang S, Yu Y, Ma D, Bridges D, Feng G and Hu A. High-performance hybrid supercapacitors on flexible polyimide sheets using femtosecond laser 3D writing. Journal of Laser Applications. 2017;**29**(2):022203. DOI: 10.2351/1.4983513

[35] Zhong C, Deng Y, Hu W, Qiao J, Zhang L, Zhang J. A review of electrolyte materials and compositions for electrochemical supercapacitors. Chemical Society Reviews. 2015;**44**(21):7484-7539. DOI: 10.1039/C5CS00303B

[36] Béguin F, Presser V, Balducci A, Frackowiak E. Carbons and electrolytes for advanced supercapacitors. Advanced Materials. 2014;**26**(14):2219-2251. DOI: 10.1002/adma.201304137

[37] Kyeremateng NA, Brousse T, Pech D. Microsupercapacitors as miniaturized energy-storage components for on-chip electronics. Nature Nanotechnology. 2017;**12**(1):7-15

[38] Parida B, Iniyan S, Goic R. A review of solar photovoltaic technologies. Renewable and Sustainable Energy Reviews. 2011;**15**(3):1625-1636. DOI: 10.1016/j.rser.2010.11.032

[39] Miyasaka T, Murakami TN. The photocapacitor: An efficient self-charging capacitor for direct storage of solar energy. Applied Physics Letters. 2004;**85**(17):3932-3934. DOI: 10.1063/1.1810630

[40] Thekkekara LV, Jia B, Zhang Y, Qiu L, Li D and Gu M. On-chip energy storage integrated with solar cells using a laser scribed graphene oxide film. Applied Physics Letters. 2015;**107**(3):031105. DOI: 10.1063/1.4927145

[41] Ren H, Lin H, Li X, Gu M. Three-dimensional parallel recording with a Debye diffraction-limited and aberration-free volumetric multifocal array. Optics Letters. 2014;**39**(6):1621-1624. DOI: 10.1364/OL.39.001621

[42] Gan Z, Cao Y, Evans RA, Gu M. Three-dimensional deep sub-diffraction optical beam lithography with 9 nm feature size. Nature Communications. 2013;**4**. DOI: 10.1038/ncomms3061