

Fabrication and Engineering of Nanostructured Supercapacitor Electrodes Using Electromagnetic Field-Based Techniques

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Over the last decade, significant efforts have been made to develop electrode architectures of the electrochemical energy storage (EES) devices. The involvement of electrostatic field, magnetic field, and electromagnetic field for electrode fabrication plays a vital role to enhance performance of supercapacitors in comparison with conventional roots. Electromagnetic techniques are advantageous over others because of several reasons including material's interactions at molecular level, noncontact energy, and chemical transportations to extract physical phase changings, and large-scale production with a cost-effective way. Recently, these techniques became a powerful tool for constructing hierarchical and well-ordered nanostructured electrodes. Their novel mechanisms and forms show high efficiency with numerous advantages such as green, simple, and mild reaction conditions. Herein, recent progress involving electromagnetic techniques for supercapacitor is reviewed; their potential future applications are also highlighted. The present review aims to serve as a guideline for fabrication techniques of next generation supercapacitor electrodes.

1. Introduction

During the last few decades, the increasing number of transistors in integrated circuits of smartphones has exceeded Moore's Law, with the steady growth rate of processor frequency over 1500% and camera pixel 5000%.^[1] In comparison, the development in smartphones battery technology is relatively slow with an annual energy density increase of only 7.2%.^[2] The slow development in battery technology thus in return prevents future advancement of smartphones. On the other hand, wearable devices with vibrant market potential have been consistently regarded as the next generation of smart technological products in the postsmartphone era. In terms of

the market value in China, the proportion of wearable electronics has increased to 471.8% in 2015 compared to the past, and this value may break 26 billion RMB in 2017.^[3,4] Under this circumstance, an unprecedented demand of ever-improving performance in accompany with novelty, scalability, and low-cost has been requested for the fabrication of electrode in smart electronics. The processing technology of electrochemical energy storage (EES) devices, however, has not yet experienced any drastic change.

Supercapacitors, as a key member of the EES family, have drawn considerable attentions due to their high power density, ultra-long cycle life, low fabrication cost, and so forth.^[5–8] In the consumable electronic market, they are complimentary to lithium ion batteries and play substantial role in driving power modules. Currently, commercially available supercapacitors are

still adopting the paste dispensing process for electrode fabrication, which dominates almost all EES production industry. However, the current technology is far from the best choice to render charge- and mass-transfer efficiency at molecular level, which is due to the inefficient mixing and uncontrollable interfaces. It is also highly dependent on the paste formulation, dispensing condition and thickness of the current collector etc.

Recently, with the development of nanotechnology, many novel materials which had not been considered before have been studied and used as electrode materials. With both opportunity and challenge, special techniques such as laser-assisted techniques, high energy ray- and particle-based techniques, must be utilized to fulfill their great potential especially in the fields of artificial intelligences, biomedical sensors, and radiofrequency identifications.^[9–12] The rising of these techniques will inevitably benefit the development of portable and wearable electronics and elevate the performance characteristics of novel module functionalities. Among these techniques, electromagnetic techniques have attracted unprecedented attentions as a result of their various merits mentioned above.^[13–20] As shown in **Figure 1**, electromagnetic techniques using for the fabrication of supercapacitor electrodes can be divided into three parts, which are electromagnetic field-based techniques, electrostatic field-based techniques, and magnetic field-based techniques. Typically, electrode fabrication techniques based on electromagnetic field can be applied to regulate properties of electrode

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materials such as bandgaps, morphologies, structures, and geometric characteristics, etc.^[13–18] For instance, microwave reaction-based techniques are very effective techniques to render porosity of nanostructured materials.^[13,14] Electrode fabrication techniques based on electrostatic field are a large group of industrialized techniques with the merits of convenience to operate, high level of security, and capability of processing controllability.^[19] According to different forms, they can be divided into electrospray deposition-based techniques, electrostatic deposition-based techniques, and electrospinning-based techniques etc., which can drive electrodes to be assembled into desirable structures and forms. Electrode fabrication techniques based on magnetic field are a novel kind of electrode fabrication technique for the application of supercapacitors.^[20] There have been many successful examples, one is utilizing magnetic field to drive nanostructured materials for assembly and alignment, the other is introducing magnetic field into the electrochemical testing process to enhance capacitive performance.

In this review article, we summarize the recent progress and advancement with respect to the application of electromagnetic techniques in supercapacitors, which have been demonstrated both effective and promising. This review aims to elucidate the principles, processes, and applications of the state-of-the-art techniques involved with electromagnetic techniques, as well as shed light on the future development of novel high-performance supercapacitors and other EESs.

2. Electrode Fabrication Techniques Based on Electromagnetic Field

Electromagnetic field is a physical field produced by electrically charged objects, which pervades in space and can be viewed as the combination of electric and magnetic fields. Electromagnetic field propagates in a wave-like manner, and expresses in the form of electromagnetic interaction which is one of the fourth fundamental interactions existed in nature.^[21–23]

Both electrostatic and magnetic fields can be distributed in vacuum, similar to air. The high voltage electrostatic field can break down air molecules and therefore can render electrochemical reactions at the surface of the electrode. The magnetic field has strong aligned force of interactions with ferromagnetic materials, which enables the alignment and aggregation of atoms. On the other hand, when an antiferromagnetic material is exposed to magnetic field, a stronger field strength is needed to render observable force interaction, such as the “levitated frog” experiment, which may initiate the structure changes on the surface of electrode materials.^[24,25]

In electromagnetism, electricity and magnetism as two expression forms of electromagnetic field, are interdependent, correlative, and supportive with each other.^[21] With the decrease in wavelength, electromagnetic waves can be categorized as radio waves, microwaves, infrared, visible light, ultraviolet rays, X-rays, and γ rays, respectively. Among them, human naked eyes can only observe visible light (wavelength: 380–780 nm).^[22]

In comparison with visible light, microwaves with a relatively longer wavelength range from 1 mm to 1 m, have been an effective technology to manufacture nanomaterials based on the effect of electromagnetic oscillation. In principle,



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electromagnetic oscillation could cause deformation and vibration of the molecules inside polar materials, so as to produce extremely fast heating and cooling rates.^[26] IR, visible, and UV light have middle wavelength ranges generated by the movement of atoms and molecules. While IR light mainly relies on the molecular rotation and vibration, visible light and UV light

Advanced Supercapacitor Electrodes Fabrication Techniques

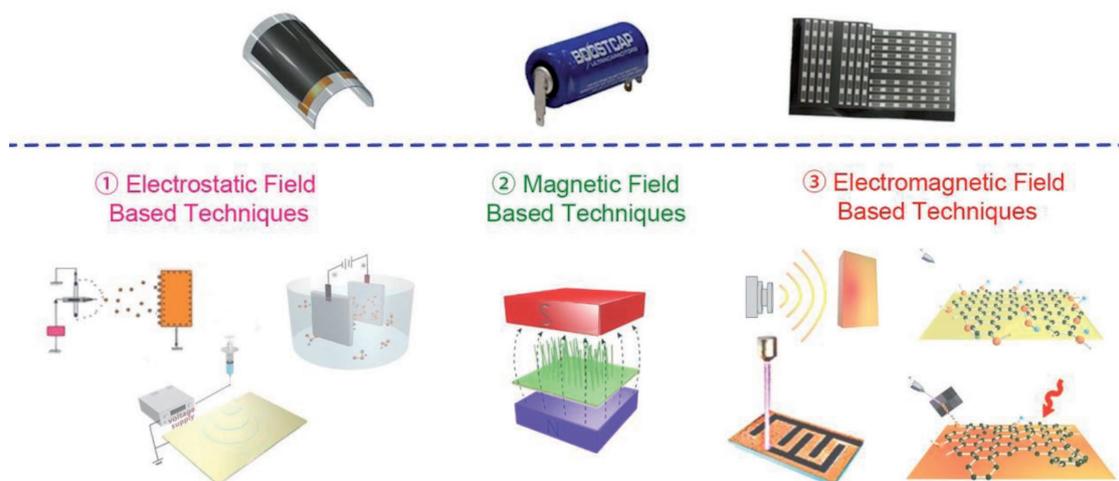


Figure 1. Schematic illustration of nanostructured supercapacitor electrodes using various electromagnetic techniques.

are mainly produced by the transition of electrons. Additionally, X-ray and γ ray featured with very short wavelengths contain flows of small particles or photon beam, possessing higher energy, can strongly render and modify electrode materials. Compared with the traditional electrode fabrication technology, the novel technologies utilizing electromagnetism can exhibit numerous advantages, such as initiation of chemical changes, highly efficient thermal-induced phase transition, nanoscale assembly and complexing, etc. All of these are prominent features which would generally endow superior electrode performance to high-performance wearable devices and high power gadgets. Photothermal, photochemical, and thermal effects can all be possibly achieved with electromagnetic field-based techniques, which can lead to profound physical and chemical changes. Due to its high efficiency, noncontact characteristic, low cost and generality, electromagnetism-involved electrode fabrication techniques have aroused great interest in recent years. For example, electromagnetic techniques have combined with different kinds of photomasks to fabricate ultrathin, lightweight, and miniature supercapacitors, which are important components for power supplementation in microelectronics. In addition, it can also be surface-mounted or embedded to a flexible printed circuit for various applications such as automatic shutting-down, miniature medical implant devices, skin induction electronic equipment, and flash-lights, which may greatly promote the development of smart technology.^[27–29]

2.1. Microwave Reaction-Based Techniques

Microwave refers to the electromagnetic wave with the energy range from 1.24×10^{-6} to 1.24×10^{-3} eV and the corresponding wavelength range from 1 mm to 1 m. It is a promising technique for manufacturing electrode materials of supercapacitors. In 1986, the first report of microwave-based synthesis method stepped into our vision, which disclosed microwave ovens as controllable thermal sources for conducting organic reactions, such as the Diels–Alder reaction, Claisen reaction, and ene

reaction etc.^[30] Meanwhile, it opened up the possibility of rapid volumetric heating at high reaction rates, short time-frame in new reactions, and the vast increase of product yields.^[30,31]

There are three interactions when microwaves encounter with materials, namely penetration, reflection and absorption. Generally, different materials have different microwave absorptive ability, which results in various degree of thermal effect. The selectivity of microwaves is determined by the dielectric loss factor, and it affects the microwaves absorption of electrode materials. Stronger dielectric loss factor causes greater absorptive capability of electrode materials. For glass, plastic and porcelain, microwaves tend to pass through rather than being absorbed. However, for water and food, microwaves are absorbed and thus heat is released. For metals, reflection is dominated. In consequence, microwave shows a characteristic of selective heating, and thus can selectively process the ingredients in a composite electrode.

In most microwave involved reactions and fabrication processes, the frequency of 2.45 GHz is widely used.^[32–34] The dielectric property of electrode materials and the electric field intensity are also significant to ascertain the average microwave power absorption value, which can be calculated by Equation (1)^[35]

$$Q_a = \omega \epsilon_0 \epsilon'' E^2 \quad (1)$$

where Q_a is the average microwave power absorption value (W m^{-3}), ω is the angular frequency (rd s^{-1}), ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), ϵ'' is the relative loss factor of the circumstance, and E is the electric field intensity (V m^{-1}). Different from conventional heating processes, more uniform products can be achieved by means of microwave radiation due to its more evenly distribution of heat. This thermal effect, from a macroscopic point of view is originated from frictional heat as a result of the rapid rotation of polar molecules under high frequency electric field generated by microwave. At the same time, the ions inside the material can convert the vibrational energy into heat under microwave field, and the

molecules can also absorb microwave energy to accumulate thermal energy.^[36]

In addition, microwave field-aided techniques process supercapacitor electrodes with the merits of high speed, uniformity, controllability due to the contribution of strong penetrability and small thermal inertia of microwave. By adjusting the output power of microwave, it is convenient to manufacture the electrodes automatically and continuously. In short, the unique characteristics of microwave reaction-based techniques includes: (i) extremely fast heating and cooling rates to produce porous nanocomposites, (ii) uniform transfer of heat to realize a more homogeneous nucleation and shorter crystallization time, and (iii) a high degree of functionalization to generate defects and introduce functional groups.^[13,26,37] Therefore, microwave reaction-based techniques for the fabrication of supercapacitor electrodes are featured with a high heat delivery efficiency to render high-performance electrode materials. With these figures of merit, this technique is especially suitable for large-scale preparation of polar electrode materials, showing great prospects in the field of portable electronic devices and field effect transistors.^[28]

In general, a porous structure is critical for supercapacitor electrode materials because it can not only increase the reactive surface area but also prompt the ion diffusion. Thus, more electroactive components can participate in the reaction, and higher current density can be achieved. Zhu et al. reported a microwave energy-assisted heating method to synthesize magnetic carbon microtubular porous nanocomposites modified by Co/Co₃O₄ nanoparticles, which ensured microwave reaction-based techniques to be a very effective means for pore-formation and structural management.^[26] Their experimental results indicated that the as-prepared microtubes exhibited an average diameter of about 10 nm and length larger than 100 nm with evenly distributed magnetic nanoparticles on microtubes. This unique open porous structure endowed efficient charge transfer between the nanoparticles and electrolyte.^[26,38,39] Until now, various unique nanostructures have been synthesized using the microwave method, e.g., Te nanorods and nanowires,^[31] ZnS and ZnSe nanowires,^[40] nanometal clusters,^[41] Bi₂S₃ and Sb₂S₃ nanorods,^[42] and so forth. These nanostructures are promising for the fabrication of various versatile supercapacitors to meet stretchable, compressible, and tailorable characteristics on the applications of electrical sensors, wearable solar cells, touch screen panel, etc. The unique nanostructure of electrode materials can be ascribed to the reduction of overall thermal gradients, which is not only conducive to both uniform nucleation and fast nanoparticle growth, but also helpful to render high porosity in the electrode structure extensively.

In a microwave-transparent reaction container, the microwave irradiation can transfer heat to the reagents uniformly, enforcing a homogeneous nucleation and shortening the crystallization time. Thus, it can reduce the adverse effects on the particle size distribution caused by unavoidable temperature gradients. Hsu et al. prepared mesoporous Ni-Co oxy-hydroxides by involving with microwave irradiation energy, which could transfer heat uniformly.^[37] The as-prepared electrode delivered an outstanding electrochemical performance, showing a high potential of microwave in the preparation of high-performance electrode materials. With this advantage,

microwave reaction-based techniques exhibit promising prospect in large-scale preparation of different metal oxide nanostructures for high-performance supercapacitor electrodes.

Among most carbon-based electrode materials, many efforts have been taken to improve the electrochemical performance via generating defects and introducing functional groups to promote the degree of functionalization.^[43,44] To date, microwave with its high fabrication efficiency and convenience has attracted people's attention more than ever in the preparation of versatile electrode materials. Microwave heating process would trigger fast reactions via in situ "super" heating to induce defect generation and oxidative functionalization, which can not only improve the electric double-layer capacitance but also enhance pseudocapacitance.^[45] Wang et al. reported highly oxidized and defective carbon nanotubes (CNTs) using microwave synthesis to enhance the performance of supercapacitors, and proposed the influence of different microwave processing time on the electrochemical properties.^[13] It turned out that the microwave treatment induced carboxylation could be achieved within 10 min. With the elongation of treatment time, electrode materials could create more defects and oxygen containing carboxylic groups. After microwave treatment, carbon-based electrode materials would have higher effective specific surface area and better electrical conductivity due to the carboxylated functionalization, which not only reduced the aggregation of carbon materials but also generated lots of defects and functional groups. Thus, a loose and porous structure could be formed, and it increased the sites for ions and electrons transferring from the electrode interface to the electrolyte. Besides, carboxylic groups would enhance the reaction sites so as to facilitate the redox reaction, which is significant for pseudocapacitance.^[46,47] Consequently, the microwave treated carbon-predicated materials utilized as supercapacitor electrodes has incredible potential for the application of intelligent arm ornaments, environmental monitoring equipment, skin induction electronic equipment etc., due to the merits of environmental cordiality and high efficiency.

To date, various microwave reaction-based techniques have been proposed to prepare high-performance electrode materials. In order to prepare porous electrode structure, Wang et al. involved microwave plasma enhanced chemical vapor deposition technique to synthesize NiO-graphene 3D composites, which revealed a higher energy and power density than the commercially available asymmetric capacitors. The excellent performance of the as-prepared electrode attributed to the highly porous architecture, which provided more active sites for accelerated electrochemical reaction.^[48] To further display the advantages of microwave reaction-based techniques, Hao et al. combined MoS₂ with Ni(OH)₂ to prepare MoS₂/Ni(OH)₂ nanocomposites via a facile single-mode microwave hydrothermal technique, as shown in **Figure 2**. Relying on the microwave irradiation, the 3D flowerlike MoS₂ could couple with Ni(OH)₂ nanoplates to form the heterostructure with a synergistic effect, which ensured a high electrochemical performance.^[49] **Table 1** gives a detailed comparison of the electrochemical performance of recent reported supercapacitors prepared by microwave heating process. Dramatically, microwave reaction-based techniques can apply to different kinds of electrode materials fabrication, exhibiting outstanding electrochemical performance.

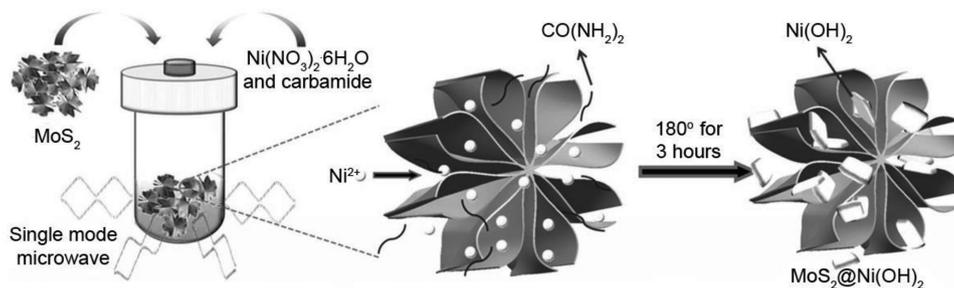


Figure 2. Schematic illustration for the formation of the self-supporting three-dimensional hierarchical nanostructure MoS₂/Ni(OH)₂ nanocomposites. Reproduced with permission.^[49] Copyright 2014, WILEY-VCH.

In addition, relying on its high process efficiency and unique characteristics described above, microwave reaction-based electrode fabrication techniques display significant potential in the manufacturing of polar compounds for microelectrode materials. These electrodes with high capacity may keep pace with the technical innovation to go with the development of high capacity storage devices, such as hybrid electric vehicles, active radio frequency identification (RFID) tags, and various kinds of sensors.

2.2. IR, Visible, and UV-Based Techniques

In addition to microwave, electromagnetic waves with shorter wavelength are also used in the construction of nanostructured electrode materials for supercapacitors. They are generally called “lights” which include IR light (wavelength: $7.8 \times 10^{-7} \text{ m} - 1 \text{ mm}$),^[57] visible light (wavelength: $3.8 \times 10^{-7} - 7.8 \times 10^{-7} \text{ m}$),^[58–60] and UV light (wavelength: $0.1 - 4.0 \times 10^{-7} \text{ m}$).^[61–63] They all belong to the intermediate energy of electromagnetic radiation region, caused by the movement of atoms and molecules. Specifically, IR light relies on molecular rotation and vibration, while visible light and

UV light are produced by the transition of electrons. As a kind of dry preparation process, light-involved techniques have emerged with remarkable advantages on the processing of electrode materials, e.g., carbon nanomaterials, and exhibit a series of features such as green, low cost, mild reaction condition, and high efficiency.

To be noted, lights can initiate the photochemical process.^[64–66] As proposed by Turro in 1978, a photochemical process means that molecules with a low energy level can absorb the quantized photon energy to attain a higher energy level, called the excited state. As a result, a series of chemical reactions can take place. When molecules are activated, their energy distribution obeys the Boltzmann distribution law, a nonequilibrium distribution. Selective excitation (i.e., the choice of jumping value, the selection of electron excited state mode, etc.), therefore, can also be achieved. Another characteristic of photochemical reaction is its independence of temperature, i.e., the electromagnetic wave can be absorbed by the material at a suitable wavelength even at a very low temperature. Therefore, the reaction pathways and the resultant products are different from the general thermochemical reaction, which would induce chemical reaction via thermal energy. In consequence, electromagnetic radiations with different wavelengths can be

Table 1. Electrochemical performance of supercapacitors prepared by microwave heating process.

Electrode material	Specific surface area [m ² g ⁻¹]	Tested current density	Specific capacitance [F g ⁻¹]	Power density	Energy density	Cycling number	Capacity retention	Year published	Refs.
NiO	176.0	5.0 A g ⁻¹	585	–	–	1000	95%	2010	[14]
RuO ₂ /GR	–	500.0 mV s ⁻¹	650	23.0 kW kg ⁻¹	57.5 W h kg ⁻¹	4000	70%	2012	[51]
MTC	–	1.0 A g ⁻¹	93	0.4 kW kg ⁻¹	8.2 W h kg ⁻¹	1000	82%	2012	[26]
Co-Ni(OH) ₂	147.7	25.0 mV s ⁻¹	636	1.6 kW kg ⁻¹	17.0 W h kg ⁻¹	–	–	2013	[37]
RuO ₂ /Si	583.0	4.0 A g ⁻¹	1152	0.7 kW kg ⁻¹	82.4 W h kg ⁻¹	–	–	2013	[52]
MoS ₂ /Ni(OH) ₂	–	2.0 A g ⁻¹	516	11.0 W cm ⁻³	5.2 mW h cm ⁻³	9000	94%	2014	[49]
GR	≈1.0	14.8 A g ⁻¹	992	14.8 kW kg ⁻¹	275.4 W h kg ⁻¹	5000	98%	2014	[50]
NiO/GR	227.7	3.0 A g ⁻¹	1829	5.3 kW kg ⁻¹	138.0 W h kg ⁻¹	5000	85%	2014	[48]
CNTs	266.0	0.1 A g ⁻¹	65	–	7.1 W h kg ⁻¹	1000	95%	2015	[13]
QNPC	–	1.0 A g ⁻¹	306	≈0.5 kW kg ⁻¹	95.7 W h kg ⁻¹	10 000	91%	2016	[53]
MEGO	937.0	1.0 A g ⁻¹	265	–	–	5000	–	2016	[54]
NHPCs	1170.0	0.2 A g ⁻¹	435	0.05 kW kg ⁻¹	9.4 W h kg ⁻¹	10 000	100%	2017	[55]
NB	–	5.0 mV s ⁻¹	123	–	–	1000	≈98%	2017	[56]

Note: CNTs, carbon nanotubes; GR, graphene; MEGO, microwave-exfoliated graphite oxide; MTC, magnetic tubular carbon nanocomposite; NB, Ni-loaded biochar; NHPCs, nitrogen doped and hierarchically porous carbons; QNPC, quasi-ordered nitrogen-enriched porous carbon.

utilized to induce various physical and chemical changes for the fabrication of multifunctional electrode materials.

Recently, the interaction between lights and graphene-based electrode materials has been intensively studied. Graphene has been regarded as a very promising electrode material for high-performance supercapacitors due to their 2D planar structure, ultrahigh specific surface area, and superior electrical conductivity.^[67,68] Visible light, UV light and IR light are a simple, green and mild process, which can make graphite oxide (GO) be reduced into reduced GO (rGO). Furthermore, compared with conventional chemical reduction methods, the light-based techniques can avoid the introduction of impurities and harsh reaction condition such as, high temperature. In general, visible light as an external field, which was first reported by Cote et al. with the merits of rapid, convenient, and clean characteristics,^[59] triggers the reduction of GO using a camera flash unit as a light source with the energy density around $0.1\text{--}2\text{ J cm}^{-2}$. Xenon light, analogous to emulated sunlight, generates heat through photothermal processes under nonradiative energy dissipation and exothermic photochemical reactions.^[58] Hence, the xenon flash light reduction mechanism of GO is similar to thermal reduction according to the decomposition of the surface oxygenic functional groups and the reformation of sp^2 domains. Moreover, a single and close-up ($<1\text{ cm}$) flash light from a xenon lamp can implement the reduction of GO and the complex with other materials simultaneously, which can expand its applications substantially. Evidences showed that flash light reduction could render corrugated and disordered rGO and lead to a high degree reduction of GO (Figure 3).^[59] Besides, functional rGO-based devices on flexible substrates by flash patterning can be produced in batch mode using a photomask. In Figure 3d, GO/polystyrene thin film with a diameter of 1.5 in.

deposited on a nylon filter paper was used to fabricate arrays of rGO/polystyrene interdigitated electrodes. Such interdigitated electrode arrays can be used not only in microelectronic devices and surface mount devices for various wearable, flexible, and portable products, but also in the applications of chemical vapor sensors, microfluidic, and electrowetting devices.^[69,70] Under flash light irradiation, GO suffers from both the photothermal conversion and heat absorption. Since both the optical absorption and heat consumption can be optimized, it can provide a positive feedback in the photothermal reduction process. Then the exposed area can be ablated to form rGO because of rapid degassing and air expansion resulted from the exposure of relatively high-power flashes. In principle, any lights within the visible spectrum can provide enough photon energy for GO reduction. Moreover, photothermally initiated exfoliation of GO can take place in an inert atmosphere. Based on the 2D reticular structure of GO, it can adsorb more energy, leading to dramatic temperature increases ($400\text{--}500\text{ }^\circ\text{C}$) within a few milliseconds upon exposure to a camera flash. Flash reduction mechanism is unique due to pulsed xenon flash with high intensity discharge lamp. It utilizes electrical stimulation to induce chemical reaction between xenon and rare earth metals, resulting in a strong photon energy that can induce deoxygenation. It can not only leads to a high efficiency, but also avoids oxygen replenishment.^[71] Therefore, a rapid and high degree of reduction of GO can be implemented by flash light for the design and engineering of nanostructured supercapacitor electrodes appropriate for versatile applications.

On the other hand, UV light as an electromagnetic irradiation source can provide higher photon energy level than visible light, and it is also a simple, environmentally benign, and low-cost method for electrode fabrication.^[61] Take GO for example, the UV light reduction mechanism of GO is via $\pi\text{--}\pi^*$ excitation of electrons, so as to generate electron-hole pairs. By the application of UV irradiation, electron-hole pairs move to the epoxy group and break C-O-C bonds of GO with the release of O_2 and the formation of relatively immense sp^2 domains occur.^[62] As shown in Figure 4, as the working medium, water exhibits a high absorption ability for UV light, which can be stimulated to form hydrogen atoms, hydroperoxyl radicals, and hydrated electrons. And the hydrated electron acting as a reducing agent can reduce GO to rGO. The only drawback is the long reaction time due to the low yields of hydrated electrons.^[16]

According to different wavelengths, UV light can be divided into near ultraviolet (NUV, photon energy: $3.10\text{--}4.13\text{ eV}$, wavelength range: $300\text{--}400\text{ nm}$), middle ultraviolet (MUV, photon energy: $4.13\text{--}6.20\text{ eV}$, wavelength range: $200\text{--}300\text{ nm}$), far ultraviolet (FUV, photon energy: $6.20\text{--}10.2\text{ eV}$, wavelength range: $100\text{--}200\text{ nm}$) and super ultraviolet (SUV, photon energy: $8.28\text{ to }124\text{ eV}$, wavelength range: $10\text{ to }100\text{ nm}$). For the case of GO, the threshold for GO reduction

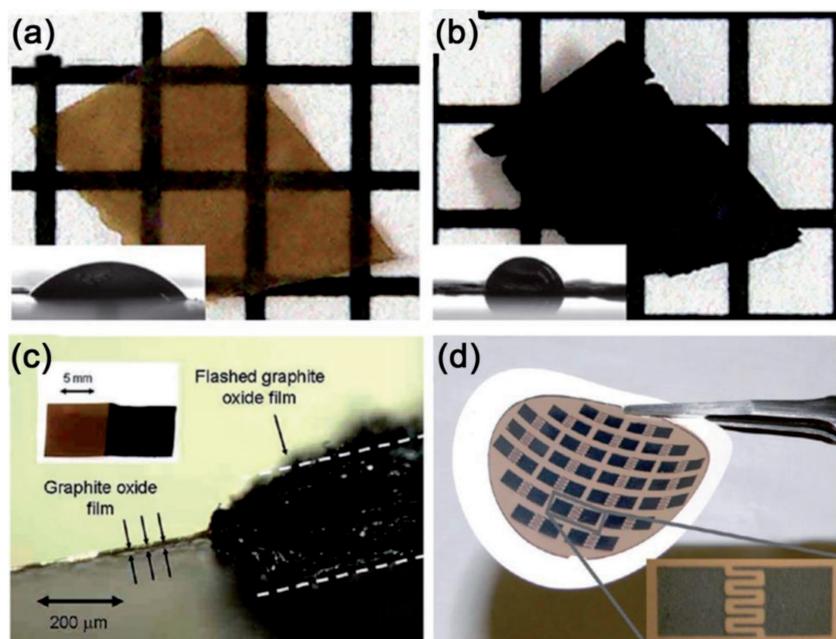


Figure 3. A GO paper a) can be instantaneously reduced b) upon exposure to a photographic camera flash. c) Cross-sectional view of a GO paper showing large thickness expansion after flash reduction. d) Scalable production of functional rGO-based devices on flexible substrates by flash patterning. Reproduced with permission.^[59] Copyright 2009, American Chemical Society.

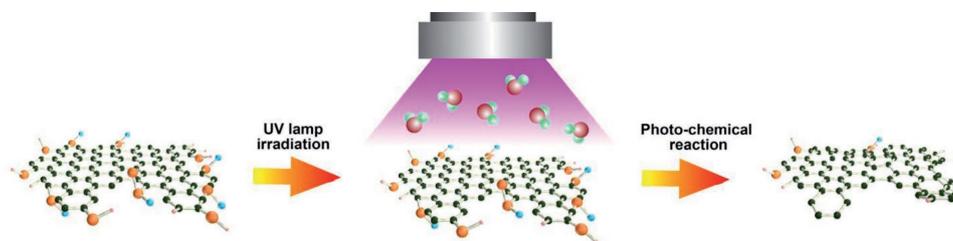


Figure 4. Schematic illustration of the reduction of GO based on UV irradiation.

requires photon energy larger than 3.2 eV ($\lambda \leq 390$ nm), then all these types of UV light can trigger the photochemical reduction of GO.^[71] Although the photon energy of NUV is lower than FUV, the penetration power is the maximum, which can influence deeper area of the material. In principle, UV light processing is a “cold processing” method, which takes advantage of the high energy of valence electrons transition to destroy materials without heating. This method can break chemical bonds of materials without causing thermal damage and also maintain their smooth edges. These edges are very opportune for precise machining of miniaturized electrode arrays, such as the antenna of RFID tags, metal mesh of one-touch screens, etc. Moreover, when the photon energy is close to the bandgap, the light absorption coefficient of materials can increase accordingly. So materials with a wide bandgap can generate more electron–hole pairs, and result in much higher electronic mobility and transport properties under UV irradiation. Besides, with the longer UV radiation time, the higher quality of electrode materials can be attained, which exhibits excellent feasibility for the fabrication of supercapacitors. In consequence, the UV-light-based techniques are quite stable and uniform processes, which show great potential in inducing phase transformation of electrode materials (e.g., graphene, transition metal carbides, and nitrides (Mxenes), transition-metal dichalcogenides (TMDs), etc.).^[72–75] While taking flexible, miniaturized, and thin-film supercapacitors into consideration, it should be a wise choice utilizing UV-light-based electrode fabrication techniques to modify these electrode materials, revealing great practical applications in smart bracelets, heart rate testing equipment, and skin induction electronics, etc. Besides, it may also find applications in the field of water splitting cells and photodetectors etc.

In addition to visible and UV lights, IR light with the wavelength of 7.8×10^{-7} to 10^{-3} m possesses the lowest reduction ability of GO due to its lower photonic energy. According to the different wavelengths, IR light can be divided into three parts, namely near infrared (NIR) with a wavelength range of 1 to 3 μm , middle infrared (MIR) with a wavelength range of 3 to 40 μm , and far infrared (FIR) with a wavelength range of 40 to 1000 μm . Comparing to FIR, the wavelength of NIR is lower, but it has better penetration ability and stronger thermal effect.

Under IR light irradiation, carbon-based materials have the remarkable capability to efficiently convert light into thermal energy through the random motion of particles. On the other hand, the coupling of the photothermal effect with the exothermic reduction can induce particles to produce thermal vibration, which is similar to microwave reaction-based

techniques that can be used to process polar electrode materials. When exposing GO to the IR light, it can release heat and gas rapidly for the expansion and development of sp^2 domains. In comparison to visible and UV lights, IR light is relatively safer due to the lower photon energy. Hence, it is suitable for large-scale fabrication of commercial supercapacitors, which can avoid involvement of protective equipment to prevent harmful radiations such as UV light. Moreover, lots of experimental results have indicated that IR light-reduced GO as supercapacitor electrodes possessed a high specific capacitance and power density, revealing a great potential in the fabrication of high-performance supercapacitors.^[17,57] Xiang et al. reported a novel FIR-based technique with the wavelength about 1000 μm to render thermal reduction process for the preparation of the FIR graphene electrode. The graphene electrode revealed an open-pore, exfoliated structure under FIR irradiation, which ensured a maximum active surface area.^[17]

Overall, the above-mentioned three kinds of electromagnetic waves all possess the virtues of ecofriendliness, simplicity, and moderate experimental conditions in the preparation of supercapacitor electrode materials, which have an enormous exploration potential. For comparison, Smirnov et al. proposed the concept of the threshold for GO reduction,^[76] i.e., visible light and IR light with longer wavelength generate photothermal effect to reduce GO through accelerating the vibration of atoms and molecules and expanding their spacing. The light irradiation techniques exhibit a significant advantage for preparing graphene-based electrode materials, but the processing temperature and the quality of electrode materials are still difficult to regulate and control. While UV light involved with higher photonic energy can render high-quality rGO efficiently via photochemical effect, whereas UV light is harmful to human health in direct exposure, which needs more rigorous personal protection in industrial electrode production. Nevertheless, the three kinds of electromagnetic waves have unique advantages in processing electrode materials. Besides graphene, some metal oxides, Mxenes, TMDs, and their derivatives may disclose a great research prospect on the fabrication of high-performance supercapacitor/pseudosupercapacitor electrodes, due to the formation of functionalized electrodes induced by light-based techniques. The as-prepared electrode materials exhibit a porous and corrugated structure, enlarging the specific surface area and conductivity, so as to significantly improve the supercapacitor performances. Relying on the high parallelism of light beams, such high-performance supercapacitors can be fabricated in a miniature size when light-based techniques are combined with photomasks, which are appropriate for all kinds of integrated circuits for the large-scale and low-cost industry

manufacture of microintelligent electronic components or sensor equipment. When dealing materials with different bandgaps, electromagnetic fields with different photon energy may play different benefits for versatile electrode materials, which are promising and meaningful for further scientific researches. Despite all this, the main technical bottleneck of light-based techniques is resulting from the control of the light source. Hence, numbers of researchers have focused on the feasibility of electrode processing by laser techniques.

2.3. Laser-Assisted Fabrication & Functionalization Techniques

Light amplification by stimulated emission of radiation, called as laser, was first mentioned by Einstein in 1916. The electrons which locate at higher energy levels can jump to lower energy levels by photon excitation or pumping effect, and it can radiate light with the same stimulated nature in the meantime, thereby forming a state of light amplification.^[77] The main characteristics of laser include excellent monochromaticity, coherence, directionality, and high luminance. The feature of coherent light means that all of its waves are synchronized. Moreover, the light intensity of laser beam is highly concentrated, so it can travel a long distance before the beam spreading or converging. Besides, laser has a well control of space and time resolution, which is especially suitable for processing object materials with a large variety of shape, nature, size, and processing condition. And thus, it can make the energy highly concentrated in the space resulting in fast absorption of concentrated radiation by electrode materials. Combining its directionality with monochromaticity, the spot size of laser can be further narrowed down to fit for refined processing. Moreover, in order to adapt large-scale industrial manufacture, lasers with different frequency can be applied at the same time according to a specified program operation combined with independent lasers. Due to the unique characteristics of laser, electrode fabrication based on laser-assisted fabrication and functionalization techniques may meet great research values and market prospects.

As early as 1960, Maiman invented the world's first ruby laser machine. Since then, laser revealed a profound technology in almost every realm. Especially, laser as an external field has been utilized in the preparation of electrode materials and could achieve self-assembly by a noncontact manner. Meanwhile it can induce physical phase changes and introduce defects, which exhibits promising application prospects in EES devices such as batteries,^[78–80] supercapacitors,^[81–89] and so on. In response to the future trend of large-scale electrode materials processing and miniaturized electronic equipment production, laser is drawing more and more attentions by virtues of its high efficiency, high quality, and low cost; while it could also achieve subtle patterning functionality under control. With various wavelength and energy density, laser has been used for processing different electrode materials such as carbon materials,^[71,78,84,85,87,88,90,91] metal oxides or sulfides,^[82,83,86,92] conducting polymers,^[93] and their derivatives or composites.^[81] When coupling the computer-based numerical control technology with a high-efficiency automatic processing equipment, it will open up a broad prospect for mass production. Particularly, micro electrode arrays fabricated by laser-based technique

trigger great prospects in energy storage devices, micropower transport systems, and medical-implanted devices, etc. In this section, we emphasize on the preparation of high-performance supercapacitor electrodes by involving laser-assisted fabrication and functionalization techniques.

On account of the specific photothermal effect and photochemical effect, graphene-based electrode materials are appealing for scientific research. Take graphene, for example, the minimum photon energy for graphite oxide reduction shall be larger than 3.2 eV, as above-mentioned.^[71] However, laser reduction may combine multiphoton absorption process in the case of some highly focused ultrafast lasers with laser-induced thermal relaxation; that is to say, it may involve both photothermal and photochemical effects. Besides, based on the unique advantages of laser, it demonstrates outstanding abilities in the fabrication and functionalization of electrode materials. The superior monochromaticity and directionality of laser provide the highly concentrated energy to modify the performance of electrode materials. Under laser radiation, the reduced graphene oxide can not only avoid the restacking of graphene layers, but also produce a porous structure.^[94,95] The level of porosity control can be well regulated by choosing different wavelength of laser sources. As Xie et al. reported the greatly expanded and exfoliated laser-processed graphene fabricated by UV laser (Nd: YAG, 355 nm).^[29] Based on this laser source, it involves both photochemical reduction pathway with the photothermal reaction, which can deliver a high photon energy over the threshold for GO reduction (390 nm, 3.2 eV) resulting to less oxidative decomposition effect of GO. On the other hand, the supercapacitors exhibit both ultrahigh energy density and excellent mechanical stability when utilizing laser-reduced graphene as electrodes, which suggests that laser as an external field involving distinctive advantages for the fabrication and integration of flexible graphene-based energy storage devices.

In 2010, Zhou et al. for the first time employed a focused laser beam technique to construct an extended area of micropatterned GO and reduced GO multilayers on quartz substrates in a fast and controllable manner.^[90] Subsequently, El-Kady et al. reported a standard LightScribe DVD optical drive to enable direct laser reduction of graphite oxide films to graphene, which revealed laser with enormous merits in the reduction of graphene oxide.^[88] The schematic illustration of the fabrication of laser-scribed graphene-based electrochemical capacitor (LSG-EC) is shown in **Figure 5a**, which demonstrated an outstanding electrochemical performance with an areal capacitance of 3.67 mF cm⁻² at a current density of 1 A g⁻¹, and maintained an excellent cycling stability up to 97% of the initial capacitance even after 10 000 cycles. Additionally, the LSG-EC could not only exhibit an energy density of 1.36 mW h cm⁻³, a value that was approximately two times higher than that of the activated carbon-based electrochemical capacitor (AC-EC), but also delivered a power density of ≈20 W cm⁻³, which was 20 times higher than that of the AC-EC and three orders of magnitude higher than that of the 500-mA h thin-film lithium battery.^[88] Moreover, Gao and co-workers found that GO could become a strongly anisotropic ionic conductor as well as an electrical insulator, enabling its use as a viable electrolyte and electrode separator, and they further demonstrated the as-prepared hydrated GO films

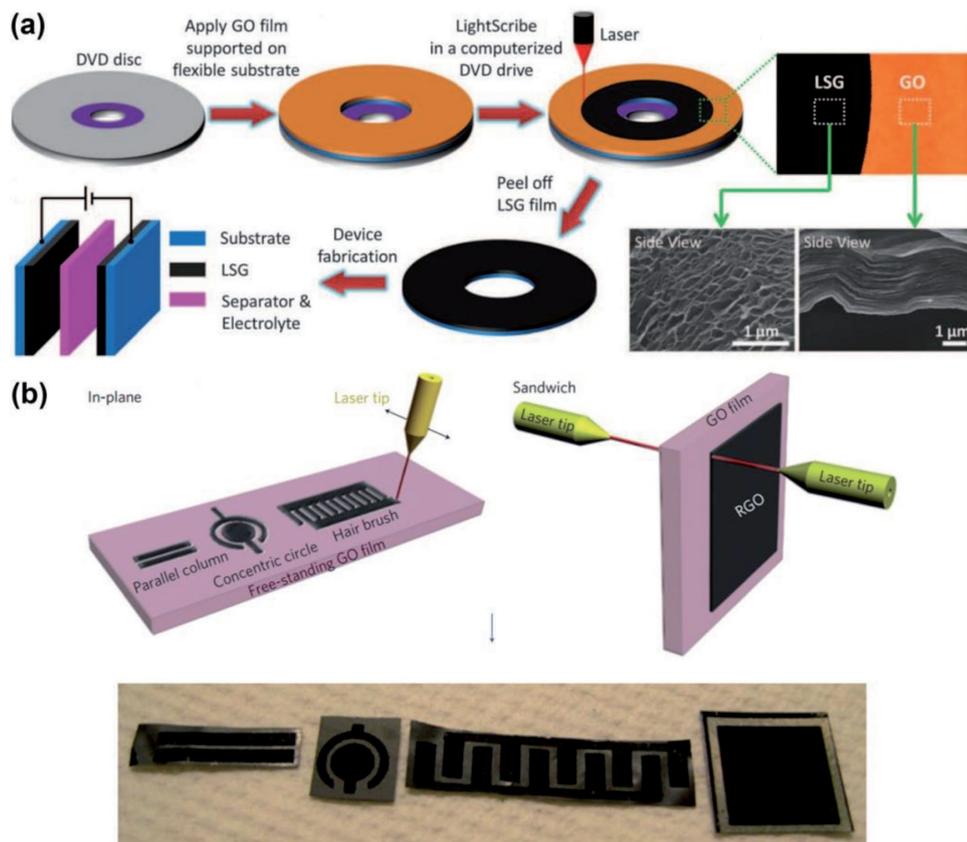


Figure 5. a) Schematic illustration of the fabrication of LSG-EC. b) Schematics of rGO-GO-rGO devices with in-plane and sandwich geometries. Reproduced with permission.^[84,88] Copyright 2012, American Association for the Advancement of Science and 2011 Nature Publishing Group.

as a novel porous solid separator/electrolyte membrane system. And then they reported the scalable fabrication of a new type of all-carbon, monolithic supercapacitor by laser reduction and patterning of graphite oxide films, as shown in Figure 5b, which showed excellent cyclic stability and energy storage ability comparable to existing thin-film supercapacitors.^[84]

Considering that the graphene-based microsupercapacitors exhibit a low areal specific capacitance on account of the mechanism of electric double-layer capacitor (EDLC),^[29] more and more researchers turn their attentions to metal oxides, metal sulfides, conducting polymers, and their derivative electrode materials, which can also be fabricated and functionalized by laser technique. Cao et al. used 2D graphene-like MoS₂ nanosheets as electrode material, which showed unique structural and electronic properties as its theoretical capacitance could attain 1000 F g⁻¹.^[82] Compared to graphene-based microsupercapacitors, the obtained MoS₂ film-based microsupercapacitors had a higher areal capacitance of 8 mF cm⁻² (volumetric capacitance of 178 F cm⁻³) in aqueous electrolytes. And it exhibited excellent electrochemical performance, which provided an efficient approach to develop high capacitive energy storage microdevices. Wang et al. reported the pulsed laser- (wavelength: 1064 nm, 10 Hz repetition rate with 8 ns pulse width) based reactive deposition technology of the NiO thin electrode film by ablating nickel targets in low-pressure O₂ atmosphere at room temperature.^[86] Under laser irradiation,

the rotating nickel target could produce energetic atoms, molecules, and ions. And then these atoms and ions underwent collisions with oxygen in the high-density region near the target, so as to generate nickel oxide molecules in the expanding ablation beam and to deposit as NiO thin film, which was about 0.12 mg in an area of 1.0 cm². Additionally, the obtained electrode showed a porous structure, which revealed a high specific capacitance of 835 F g⁻¹ at a current density of 1 A g⁻¹ and an excellent cycling performance (94% capacitance retention after 1000 cycles). On the other hand, laser has been used for patterning conductive polymer electrodes as early as 2007.^[93] Acevedo et al. demonstrated micro/nanometer-sized polyaniline (PANI) arrays fabricated by direct laser interference (wavelength: 355 nm) to produce micro- and even nanoscopic patterns on a large area. Moreover, they found that PANI electrode arrays could be ablated through the photothermal process. And the multilayer structures could be built by regulating the laser wavelength and intensity, which realized a controllable patterning process on a broad range of polymer substrates. In consequence, under laser irradiation, metal oxides, metal sulfides, conducting polymers and their derivative electrode materials can provide more benefits in both specific capacitance and volume energy density. All above demonstrate that laser irradiation is a very promising technique in the fabrication of microelectrodes for high-performance supercapacitors. Such laser-fabricated supercapacitors can be integrated in many

technological developments such as, printed circuits, active RFID tags, and miniature wearable electronics.

In consequence, laser reduction of GO can produce porous structure to promote ions/electrons transfer between electrolyte and electrode, which does not involve with either high temperature or toxic chemicals. Moreover, laser reduction of GO permits exquisite control over film conductivity, residual oxygen content, and surface wettability, which can lead to various functionalities toward a wide range of applications. Except for carbon-based electrode materials, some metal oxides, metal sulfides, conducting polymers and their derivatives may have a more broad application prospect for fabricating interdigitated microsupercapacitors with a higher capacitive performance due to the mechanism of pseudocapacitance. In order to meet the future demand, the most possible and significant directions for laser in the application of supercapacitor may include three aspects: (i) utilizing the elaborate design of laser patterning does not involve the use of any predefined patterned substrates, and is easier for the fabrication of state-of-the-art supercapacitors with various complex patterns or micrometer-sized feature, superior to photolithography and stencil printing et al. For example, Shi et al. prepared supercapacitors with a “Chinese panda” pattern via complicated screen-printing;^[96] as compared, Xie et al. utilized laser-assisted fabrication and functionalization technique that could not only easily render the aesthetic characteristic of supercapacitors, but also highlight the shape versatility of supercapacitors for the wearable, portable, and other consumer electronics, such as Apple iPhones and a Jawbone smart bracelet (**Figure 6**);^[29,97] (ii) laser-assisted fabrication technologies can realize scalable fabrication of high-power microsupercapacitors for flexible, portable, and on-chip energy storage applications to keep up with the commercial substantial electronics production;^[8,70,98,99] (iii) it provides an effective functionalization tool in the surface modification of electrode materials, which introduces defects and induces a

localized physical state transition so as to greatly improve the electrochemical performance.^[92,100]

In summary, laser as a unique kind of electromagnetic wave with excellent monochromaticity, coherence, directionality and high luminance reveals lots of merits. Based on laser-assisted fabrication and functionalization techniques, we can fabricate ultrathin electrodes and interdigitated electrode arrays for flexible supercapacitors and microsupercapacitors. Also, laser techniques can be utilized to process thicker electrodes with a high mass loading and induce phase transformation of electrode materials for high volumetric energy density and outstanding properties. Therefore, it provides an excellent opportunity to develop various electronic components such as wearable electronic devices, miniature skin sensors, environmental monitoring equipment and so on, to meet the needs of smart homes and home automation. Currently, further studies regarding the interactions between laser and these electrode materials may attract a broad research interests. Laser is becoming an effective and powerful technology in driving assembly of nanostructured electrodes for high-performance supercapacitors.

2.4. High Energy Ray- and Particle-Based Techniques

In addition to the above-mentioned electromagnetic field-based techniques, there is another kind of novel technique, i.e., high energy ray- and particle-based technique, which consists of the flow of a bunch of small particles or photon beams with specific energy higher than that of light. Here, we emphasize on several kinds of high energy ray- and particle-based techniques in the contribution of nanostructured supercapacitor electrodes fabrication, including X-ray, γ -ray, electron beam, and plasma-based techniques. Although electron beam and plasma do not belong to electromagnetic radiation, they are classified in this chapter due to their high energy nature and similar processing technology. High energy ray and particle irradiations with strong penetration ability can be generated by the aid of a ^{60}Co source, nucleus, neutron, electron, or other accelerated ions and so on. It can utilize the interaction between rays and materials to ionize and stimulate the activation of atoms and molecules so as to generate a series of physical, chemical, and biochemical changes, resulting in polymerization, modification, and degradation of materials.^[17]

Among these techniques, X-ray has its wavelength ranging from 0.01 to 10 nm, corresponding to frequency in the range of 3×10^{19} to 3×10^{16} Hz and energy in the range of 100 keV to 100 eV. Since X-ray wavelength is shorter than visible light, UV light, IR light and microwave, each photon can carry more energy to ionize atoms and disrupt molecular bonds. Therefore, X-ray can be used to probe the microstructure of materials. Similarly, γ -ray has even shorter wavelength, while it is a kind of penetrating electromagnetic radiation arising from the radioactive decay

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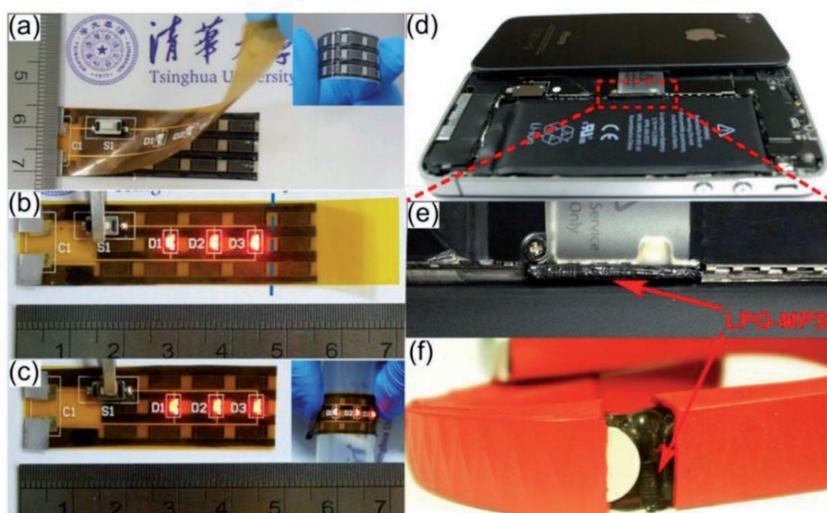


Figure 6. a–c) Photographic images of three pieces of light emitting diodes driven by laser-processed graphene-based microplanar supercapacitor (LPG-MPS) array in the state of tailor and bending. d–f) Ultrathin flexible LPG-MPS array was tucked into the seam in iPhone 4 and a UP24 smart bracelet. Reproduced with permission.^[29] Copyright 2016, Elsevier Ltd.



Figure 7. Schematic illustration for preparing hierarchical rGO/aMWCNT composites under γ -ray irradiation. Reproduced with permission.^[105] Copyright 2013, Elsevier.

of atomic nucleus, and therefore it consists of high-energy photons. γ -irradiation is the decay of an atomic nucleus from a high energy state to a lower energy state, which is called γ decay. In principle, the frequency of γ -ray is above 10^{19} Hz, energy more than 100 keV, and wavelength less than 10^{-11} m, which is less than the diameter of an atom. Similar to X-ray, γ -ray is also ionizing radiation, which is biologically hazardous. Electron beam (also called cathode ray) is a stream of electrons that can be observed in vacuum tubes, which travels along straight line with a high-energy density. In this section, X-ray, γ -ray, and cathode ray belong to high energy rays, techniques based on these rays reveal many advantages, such as being chemically reductant-free, environmentally friendly, cost-effective, and easily scalable.^[101,102]

At present, there have been few reports about ray-based techniques in the fabrication of supercapacitor electrode, such as the reduction of GO for preparing electrode materials.^[103–105] Electron beam-based techniques can cause the reduction of GO at room temperature under ambient air condition due to its high energy density.^[106–108] However, electron beam irradiation rapidly decays and deposits most energy on the surface of samples, which limits the treatment area, depth, and uniformity. By contrast, both X-ray and γ -ray possess shorter wavelengths and higher energy levels, and a much deeper penetrating distance could be achieved through the material, and these have been used to prepare or modify metallic nanoparticles,^[109] CNTs,^[110,111] and fullerene.^[112] These two techniques can also introduce defects and cause quick and comprehensive chemical and physical changes to electrode materials owing to their high energy level. Although γ -ray irradiation has various advantages for radiolysis, it must be carried out under oxygen-free conditions because γ -ray can be significantly suppressed by oxygen quenching process in the air.^[102,113] These rays-based techniques can provide an efficient method for large-scale production of graphene, which can exhibit a vast range of applications in the field of energy storage, energy conversion, and photodetection.

In 2014, Cai and co-workers developed a simple and environmental friendly approach to prepare graphene electrode, by γ -ray irradiation inducing the reduction of GO at room temperature with the addition of surfactants. Thus GO was reduced by the electrons generated from the radiolysis of *N*-methyl pyrrolidone (NMP), and the rGO was simultaneously functionalized

by the radiolytic product of NMP. The as-prepared graphene/PANI composites were used as supercapacitor electrode materials, showing a high specific capacitance of 484 F g^{-1} at a current density of 0.1 A g^{-1} .^[103] Sun and co-workers reported the reduced graphene oxide/acid-treated multiwalled carbon nanotube composites (rGO/aMWCNT) as supercapacitor electrode prepared by ^{60}Co γ -ray irradiation, which possessed high conductivity (1820 S m^{-1}), large specific surface area ($1420 \text{ m}^2 \text{ g}^{-1}$) and low oxygen content (Figure 7). Besides, it showed improved electrochemical capacitance with a specific capacitance of 227 F g^{-1} and excellent cycling stability with 4.9% capacitance loss after 10 000 cycles.^[105] The possible mechanism of GO reduction was proposed. During the irradiation reduction process, alcohol radicals ($\text{R}_1\text{R}_2\text{-COH}$) firstly attacked the oxygen atoms of epoxide groups in GO, where the ring-opening reactions could take place. After that, hydrogen radicals (-H) were combined with carbon radicals, resulting in the formation of C–H bonds. At last, the elimination reactions between the generated $\text{R}_1\text{R}_2\text{C(OH)O-}$ and H-groups took place, and the C=C bonds were produced through the removal of gem-diols [$\text{R}_1\text{R}_2\text{C(OH)}_2$]. Because $\text{R}_1\text{R}_2\text{C(OH)}_2$ was very unstable and could readily transform into ketone (or aldehyde) and water, the reduction of GO could be achieved thoroughly. For systematically investigating the effect of electron beam irradiation dose on the physicochemical properties such as disorder degree, oxygen content, pore structure, specific surface area, sheet resistance, and electrochemical performance of supercapacitors, Kang and co-workers successfully obtained rGO with abundant micropores by electron beam irradiation at room temperature under ambient air condition. In their experiment, the highest capacitance of the reduction of GO was achieved 206.8 F g^{-1} at a charge/discharge current density of 0.2 A g^{-1} in 6.0 M KOH aqueous solution for a sample reduced by electron beam irradiation of 200 kGy .^[102]

Besides high energy ray-based techniques, high energy particle-based techniques/plasma-based techniques, also provide a unique medium for enabling reactions and modifications of nanostructures becomes compelling in recent years. Plasma is one of the four fundamental states of matter which mainly consists of electrons, ions, free radicals, neutral particles and photons with specific energy. The active free radicals can trigger chemical reactions; and the charged atoms and molecules can provide physical bombardment effect, i.e., sputtering.

Considering these two aspects, plasma-based techniques can effectively modify a large variety of material surfaces, rendering surface functionalization, defects induction, pollutants removal, etching effect and so on, which makes it an indispensable tool.^[114–117] Notably, plasma with the unique ability can not only virtually break down any hydrocarbon-containing precursors in a different state of matter (i.e., solid, liquid, or gas) and reconstruct them into functional nanostructures, but also produce defects through the strong plasma–matter interactions and induce vertical orientation of the materials via the electric-field-guided growth in the plasma sheath.^[118–120]

To date, plasma-based techniques have been used in the design and engineering of nanostructured supercapacitor electrodes; Ar, CH₄, H₂, N₂ and their mixtures have been used as the plasma sources.^[121–128] For instance, Zhang et al. proposed a fast, effective, and environmental-friendly method to prepare 3D porous hierarchical structured metal nitrides (NiMoN), using radio frequency (RF) sources to generate nitrogen plasma in a plasma-enhanced chemical vapor deposition (PECVD) system (**Figure 8**).^[121] The nitrogen plasma was mainly composed of excited states of N₂, N₂⁺, and N species. The energetic nitrogen ions caused the sputtering of Ni–Mo particles resulting in sputtered Ni and Mo atoms reacted with excited nitrogen atoms, and then recrystallized to produce the Ni_{0.2}Mo_{0.8}N phase. The results showed that the obtained 3D hierarchical porous materials could exhibit outstanding hydrogen evolution reaction (HER) electrocatalysis application. In order to further lower production cost, cheap and abundant Co₃O₄ nanosheets have been used as oxygen evolution reaction (OER) electrocatalyst through bandgap engineering by N₂

plasma treatment, showing advanced electrocatalytic performance.^[122] More importantly, electrode materials processed by plasma-based technique revealed porous functionalization nanostructures and lots of defects, which greatly increased the specific surface area and reaction sites resulting in ultrahigh electrochemical performance. For example, Zhu et al. combined Ar⁺ plasma etching with N-doping to induce defects in the few-layer graphene structures, which significantly improved the measured capacitance and the energy density.^[123] Xu et al. demonstrated an improved supercapacitor performance based on 1D anodic titanium oxide (ATO) nanotube arrays through selective plasma-assisted hydrogenation (ATO-H).^[124] The increased charge storage capacity was ascribed to the highly roughened surface induced by the plasma-etching effects. Compared to the conventional methods, plasma-based techniques may be a superior choice to fabricate electrode materials (e.g. transition-metal phosphides (TMPs), transition-metal borides (TMBs), and transition-metal fluorides (TMFs)) at low temperature and in a rapid manner, which can not only reduce cost but also improve the performance of electrodes.^[129] Hence, plasma-based techniques provide great prospects in the modification and functionalization of electrode materials, which have a great potential to fabricate water splitting cells, ultrahigh power supercapacitors for the applications of automatically shutting-down, automatic doors, brake systems, and the forth.

In conclusion, high energy ray- and particle-based techniques including X-ray-based techniques, γ -ray-based techniques, electron-beam-based techniques, and plasma-based techniques are a kind of novel and efficient strategy to fabricate functionalized

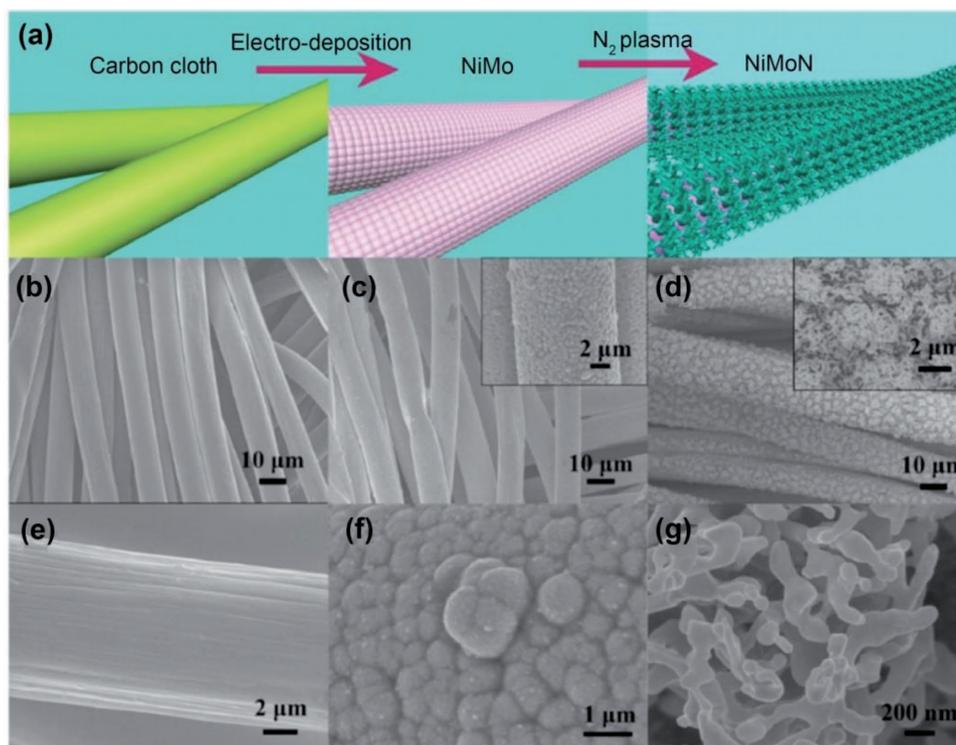


Figure 8. a) Schematics of the fabrication process of 3D hierarchical porous NiMoN. b–e) SEM images of carbon cloth. c–f) NiMo alloy deposited for 7200 cycles. d–g) NiMoN treated under nitrogen plasma for 15 min. Reproduced with permission.^[121] Copyright 2016, WILEY-VCH.

nanostructured materials, by which supercapacitor electrodes may meet superior electrochemical performance. X-ray-based techniques, γ -ray-based techniques, and electron beam-based techniques are also competitive solutions for the production of high quality and conductive graphene electrodes. Nevertheless, high energy ray-based techniques have harmful effect on human health, and have to involve protective equipment in the fabrication processes. Besides, it is still difficult and expensive to utilize ray-based techniques in the large-scale production of electrode materials, especially γ -ray is restricted to inert atmosphere, which seriously affects the industrial electronic applications. Anyway, there is no doubt that high energy ray- and particle-based techniques have great prospects in breaking chemical bonds and creating various defects for porous and high specific surface area electrode materials, which are feasible for grid-scale applications in bioelectronics with special functions, catalysis, electronic monitoring equipment, etc. High energy ray- and particle-based techniques as technical supplements also reveal significant value for supercapacitor electrode fabrication techniques.

3. Electrode Fabrication Techniques Based on Electrostatic Field

Electrostatic force is the interaction force between charged bodies. Electrostatic field-based techniques provide us low-cost, highly effective, and optimal condition in developing high-performance miniaturized EES devices. The future intelligent and portable electronics critically require energy storage devices with superior mechanical performance characteristics, such as flexibility, rollability, and stretchability. Electrostatic field technique is very suitable for preparation of thin electrodes, which can be used for fabrication of flexible electronics. Moreover, based on the flexible electrodes, we can even fabricate a series of artistic patterns for various wearable devices, and miniature interdigital arrays for on-chip integration and intelligent electronic devices, through combining with photolithography technique or laser technique.^[96,97,130] These techniques are inexpensive and scalable for industrial purpose and can easily be applied for mass production.^[131] In this section, we emphasize on three types of electrode fabrication techniques based on electrostatic field, including electrospray deposition-based techniques, electrostatic deposition-based techniques, and electrospinning-based techniques. The following paragraphs will discuss in details about their applications in the fabrication of supercapacitor electrode.

3.1. Electrospray Deposition-Based Techniques

Electrospray deposition-based techniques, also called electrostatic spray deposition (ESD) techniques, are a method of liquid atomization that uses high voltage electrostatic field to make negatively charged particles moving along the electric field in the opposite direction, and then the coated particles will be adsorbed on the surface of substrate.^[132] ESD techniques have the characteristics of easy operation, high efficiency, environmental friendliness, low cost, and the excellent control on size

and charge of droplets by external field in order to get homogeneous distribution and controllable thickness. Moreover, ESD techniques have a wide operating window, resulting in a high electric field intensity. It can induce assembly of low-dimensional nanomaterials by solvent evaporation, which is beneficial for the preparation of supercapacitor electrodes. Nevertheless, on account of the effect of electrostatic force field, ESD techniques are significantly influenced by processing parameters such as dielectric environment and viscosity of liquid. To date, ESD techniques have been widely used in the fabrications of thin film supercapacitors,^[132–134] microsupercapacitors,^[29,135,136] solar cells,^[137] fuel cells,^[138,139] and batteries^[140,141] involving the application of graphene,^[134] graphene oxide,^[17,29,142] carbon nanotube,^[133,136] and carbon-based composites,^[135,140,141,143] etc.

Notably, graphene as a typical representative has been widely applied on various EES devices utilizing electrospray deposition-based techniques. One of the unique characteristics of ESD technique is that, it can eliminate the involvement of conductive agents and binders along with reduction in the aggregation effect of graphene. This is beneficial for the formation of 3D porous graphene-based electrode materials to enhance its electrochemical performance, owing to the strong electrostatic repulsion effect and solvent evaporation of ESD techniques. Besides carbon-based materials, metal oxides, metal sulfides, and their derivatives (e.g., MnO_2 , MoS_2 , MoTe_2 , MoSe_2 , etc.) used as electrode materials prepared by ESD-based techniques shall also reveal a great prospect for the applications of supercapacitors. However, the biggest challenge may be the material dispersion in liquid phase. The suitable solvents should be chosen to disperse these electrode materials correspondingly. Different from the above electromagnetic field techniques, ESD techniques have been more thoroughly studied for precursor fabrications for electrode materials rather than directly changing the nature of them. It is a unique way to get thin, homogeneously dispersed, and thickness-controllable precursor materials. Hence, it is more likely to combine ESD techniques with other methods to develop high-performance electrode materials.

In 2012, Beidaghi et al. first reported the graphene electrode film via ESD preparation technique. Based on the ESD technique, it is easy to prepare ultrathin graphene electrodes with 1 μm thickness, which are promising candidates for the applications of thin-film energy storage.^[134] It is worth mentioning that GO sheets can be directly reduced to rGO during the process of ESD. In order to further promote the advantages of ESD techniques, Beidaghi et al. also fabricated reduced graphene oxide and CNTs composites for ultra-high power microsupercapacitor application. The interdigitated rGO–CNT composite electrodes showed an unprecedented performance for supercapacitors, indicating electrospray deposition-based techniques are promising for the fabrication of high-performance electrodes.^[135] The morphology and thickness of the deposited film can be controlled by adjusting the ESD parameters such as the applied potential, flow rate of spray solution, substrate temperature, and composition of the precursor solution.^[144]

Usually, the precursor for the ESD process is a compound, which can be decomposed to the desired material at a high temperature during deposition^[142] or calcination after deposition,^[140,141] or combining with radiation method,^[17] vapor

deposition polymerization,^[143] photolithography lift-off methods,^[135] laser-processing,^[29] and so forth to fabricate the required electrode materials. Yin and co-workers designed and assembled the Si/C nanoporous microspheres via electro-spraying the aqueous solution containing silicon nanoparticles and sodium alginate in a CuCl_2 solution, followed by calcination to realize carbonization.^[140] The results demonstrated the importance of nanopores and electronically conducting coating layers for the enhanced electrochemical properties of Si-based electrode materials. Notably, ESD is an effective technique to produce nano/microspheres for electrode materials without the use of hard templates. The electro-sprayed microspheres, capable of size modulation in the micrometer region, are conveniently prepared on the basis of using an electrostatic field between a capillary tip such as a nozzle and a flat counter electrode. Wang and co-workers for the first time made Sb nanoparticles encapsulated in 3D reticular carbon by ESD technique, followed by a heat treatment, and demonstrated a facile and versatile technique to prepare a reticular porous electrode structure with excellent electrochemical properties.^[141] Xiang and co-workers reported a novel FIR thermal reduction process combined with ESD technique to effectively reduce graphene oxide films for supercapacitor electrode applications.^[17] Lee and co-workers reported the fabrication of Fe_3O_4 /carbon hybrid nanoparticles using dual-nozzle electro-spraying incorporating with both vapor deposition polymerization and carbonization. During the electro-spraying process, the high and positive voltage applied enabled uniform dispersion of Fe^{3+} ions on the polypyrrole surface, so as to lead to a uniform and nonaggregation structure, resulting in a high specific capacitance of 455 F g^{-1} and a better cycle stability during charge-discharge cycling.^[143]

In order to further investigate the feasibility of utilizing ESD-based techniques, Yang and co-workers reported the involvement of ESD techniques on the application of supercapacitors, highlighting the merits of ESD techniques in preparation of uniform thin film or miniaturized electrodes. They prepared 3D porous crumpled graphene electrodes (C-rGO) for supercapacitor electrode application by the ESD method, and the schematic illustration is shown in **Figure 9**.^[142] An electric furnace was used to accelerate the evaporation of the solvent, which was placed at the bottom of the region between the nozzle and the

collector. A syringe pump was utilized to let graphene oxide suspension feed into a stainless steel nozzle at a feeding rate of 0.15 to 0.30 mL min^{-1} . The working voltage was set in the range of 30 – 35 kV , and the distance between the substrate and nozzle was controlled at 25 cm . Due to the introduction of an electric furnace, the aerosolized GO particles started the crumpling process resulting from rapid evaporation. And then, C-rGOs were deposited uniformly on the stainless-steel collector. The thickness of C-rGO layer can be adjusted conveniently by tuning the deposition time, surface tension of the suspension, voltage and pumping rate. After that, the symmetric supercapacitor exhibited excellent specific capacitance (366 F g^{-1} at 1 A g^{-1} in 6 M KOH) and long cycle life (108% capacitance retention up to $40\,000$ cycles). Moreover, the energy densities of the organic and aqueous electrolyte-based supercapacitors could reach 22.9 and 8.1 W h kg^{-1} , respectively, when the power densities are 119.2 and 15.4 kW kg^{-1} , respectively. Furthermore, Yang's group combined ESD with laser processing technology to fabricate graphene-based microplanar supercapacitors. As shown in **Figure 10**, ESD technique can ensure a homogeneous coverage of GO with adjustable thickness, which is beneficial to achieve a high quality microsupercapacitor electrode. As compared to a commercial surface mount microsupercapacitor product and an aluminum electrolytic capacitor product, the rGO electrode-based microsupercapacitor showed outstanding rate performance, excellent cycle stability and high volumetric energy density ($0.98 \text{ mW h cm}^{-3}$ in LiCl-polyvinyl alcohol aqueous gel, 5.7 mW h cm^{-3} in ionic liquid). In addition, it is likely to utilize the microsupercapacitor arrays to mount on flexible printed circuit for potential applications in smartphones, smart bracelets, and other consumer electronics.^[29]

In a word, ESD-based techniques can prepare porous, thin, uniform, thickness-controllable electrodes; it is a cheap, scalable, and highly reproducible technique. Especially, ESD techniques can not only eliminate the involvement of conductive agents and binders, but also minimize the aggregation effect of the sprayed matter, e.g., graphene, which makes it a general method for the preparation of graphene analogues and composite materials with a porous structure. Besides carbon-based materials, we expect that 2D electrode materials such as MoS_2 , MoTe_2 , MoSe_2 , MXenes, C_3N_4 , and black phosphor etc., fabricated by ESD shall also reveal a great prospect for

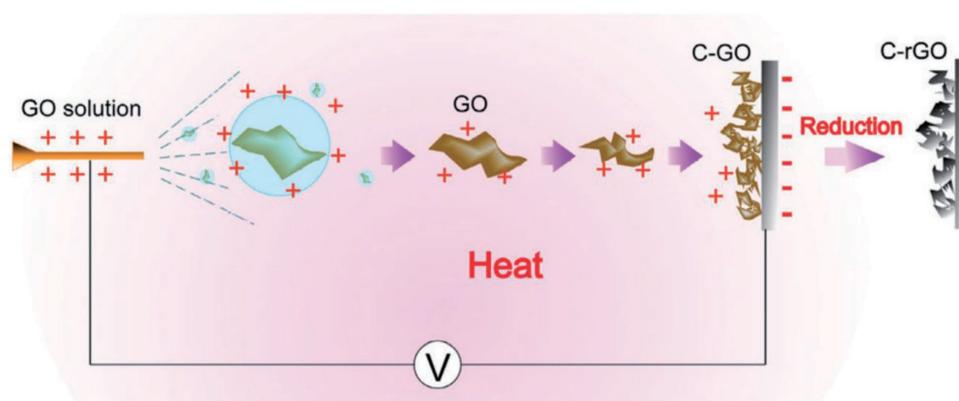


Figure 9. Schematic illustration of the process for fabricating C-GO and C-rGO. Reproduced with permission.^[142] Copyright 2015, The Royal Society of Chemistry.

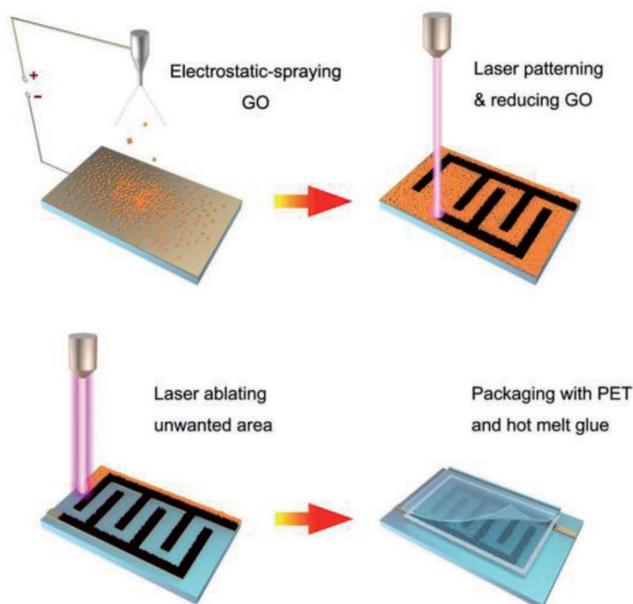


Figure 10. Schematic illustration of ultrathin laser-processed graphene-based microplanar supercapacitors. Reproduced with permission.^[29] Copyright 2016, Elsevier.

the application of supercapacitors. Additionally, it is obvious that combining ESD techniques with other methods such as thermal decomposition, vapor deposition polymerization, laser-processing etc. can address various kinds of functionalized electrode productions for the applications of high-performance supercapacitors. While main shortcomings of ESD still hinder its broader application in industry, such as the relatively low throughput. Therefore, multiple nozzles and ventilations shall be involved for mass production. Nevertheless, we believe that ESD techniques hold a great promise in the preparation of various precursor electrode materials for thin film supercapacitors and microsupercapacitors, which meet broad applications in various touch screens, optoelectronic devices, flexible printed circuit boards, and so on.

3.2. Electrostatic Deposition-Based Techniques

Similar to ESD-based techniques, electrostatic deposition-based techniques are also enabled by the existence of electric field. However, the main working environments of electrodeposition are carried out in either aqueous or organic solutions; and the working voltage is quite low because of the risk of solvent decomposition. Electrostatic deposition-based techniques show lots of merits, such as very simple, reliable, controllable, economic, ecofriendly and versatile, which have been extensively employed to prepare nanostructured electrodes for high-performance supercapacitors.

With the presence of electric field, the electrostatic deposition processes can take place in an electrolytic cell, which enables the ions in the electrolyte solution to deposit on the surface of the cathode or anode to form a coating layer. As the electrochemical reactions are carried out on the surface of electrode materials, the electron transfer processes take place concurrently, making

the molecular or atomic level deposition possible and the corrosion process controllable as well. With enormous advantages of electrostatic deposition-based techniques, they have been extensively investigated and applied in various energy storage fields, especially in the electrode preparation of nanostructures and thin layers. Besides, it can be employed in various complex substrates for uniform deposition, which is suitable for all kinds of shapes of substrate materials, such as the contoured surfaces. Electrodeposition is a process by which a thin and adherent coating of metals,^[145] metal oxides or hydroxides,^[6,19,131,146–149] polymers,^[150–153] carbon-based materials,^[154] or their composites^[155] can be formed on the surface of a conductive substrate, via a simple electrolysis of a solution containing the desired metal ion or its chemical complex. Through changing the electrochemical conditions, e.g., current density, electrodeposition potential, pH value of the electrolyte, temperature, electrolyte composition and deposition time, the deposited materials can be precisely controlled with the thickness, composition and nanostructure.^[156]

On the other hand, it is worth mentioning that another liquid phase deposition techniques, electrophoretic deposition (EPD) technique, exist physical changes but not necessarily with chemical reactions. However, the electrostatic deposition process can occur with chemical reactions, and the valence electrons can transfer between electrolyte and electrode materials. EPD is a process that colloidal particles suspended in a liquid medium migrate under the influence of an electric field and can be deposited onto an electrode. With increased attention both in academia and industrial sectors, EPD is widely used in the preparation of supercapacitor electrodes because of the cost-effectiveness and the requirement of simple apparatus.^[157–162] In addition, the coating prepared from EPD has a strong adherence to the substrate, together with high density and excellent homogeneity.^[163] In comparison, the basic difference between EPD and electrostatic deposition-based techniques is ascribed to the fact that the former is based on the suspension of particles in a solvent whereas, the latter is based on a solution of electrolytes. However, both of these techniques are scalable and inexpensive ones in industrial process which can produce a very uniform film of electrode materials.

To date, a series of highly conductive substrate materials have been employed as scaffolds to deposit various electroactive materials, which showed large surface area, high electric conductivity and excellent capacitance performance, as shown in **Table 2**. Fan and co-workers utilized a hierarchically porous carbon monolith as the backbone to support PANI by the potentiostatic deposition, with the advantageous of high stability and high performance, which greatly highlighted the prospects of electrostatic-deposition-based techniques for the applications of low-cost, scalable supercapacitors.^[150] In 2014, Xiao et al. developed a facile method to prepare highly conducting NiCo₂S₄ nanotube arrays as scaffold to deposit electroactive materials, such as Co_xNi_{1-x}(OH)₂, MnO₂, and FeOOH. Relying on the unique porous nanostructure of NiCo₂S₄, the electrodeposited electrode materials revealed superior electrochemical performance, which further disclosed the great potential of electrostatic deposition-based techniques in the field of energy storage.^[6]

Table 2. The electrode materials prepared by electrostatic deposition and its electrochemical performance.

Electrode materials	Substrate materials	Current density	Specific capacitance	Power density	Energy density	Cycling number	Capacity retention	Year published	Refs.
Co, Ni, Fe	CNW	–	–	–	–	–	–	2002	[145]
PANI	CM	0.7 A g ⁻¹	2200 F g ⁻¹	≈0.5 kW kg ⁻¹	300.0 W h kg ⁻¹	–	–	2007	[150]
MnO ₂	CNTs	–	199 F g ⁻¹	–	–	20 000	97%	2008	[146]
MnO ₂	GRT	2.0 mV s ⁻¹	315 F g ⁻¹	110.0 kW kg ⁻¹	12.5 W h kg ⁻¹	5000	95%	2011	[147]
MnO ₂	GR	2.0 mV s ⁻¹	130 F g ⁻¹	62.0 W kg ⁻¹	6.8 W h kg ⁻¹	5000	80%	2012	[148]
PANI	GR	2.5 A g ⁻¹	970 F g ⁻¹	–	–	1700	90%	2012	[151]
NiCo ₂ O ₄	NF	2.0 A g ⁻¹	2010 F g ⁻¹	–	–	2300	94%	2012	[149]
MnO ₂ / PEDOT:PSS	SSM	0.5 mA cm ⁻²	1670 mF cm ⁻²	0.4 W cm ⁻³	1.8 mW h cm ⁻³	4000	≈99%	2013	[19]
MnO ₂	NCA	2.0 mV s ⁻¹	632 F g ⁻¹	2.0 kW kg ⁻¹	52.2 W h kg ⁻¹	20 000	≈95%	2014	[131]
Co _x Ni _{1-x} (OH) ₂	NiCo ₂ S ₄ NA	4.0 mA cm ⁻²	≈3 F cm ⁻²	–	–	2000	96%	2014	[6]
Ppy/MnO ₂	CC	20.0 mA cm ⁻²	≈60 F cm ⁻³	1.3 W cm ⁻³	27.0 mW h cm ⁻³	5000	96%	2015	[155]
GR	NCA	2.0 mV s ⁻¹	57 mF cm ⁻²	4.0 mW cm ⁻³	0.2 mW h cm ⁻³	20 000	99%	2015	[154]
Co-Ni-DH	NF	5.0 mV s ⁻¹	1201 F g ⁻¹	11.6 kW kg ⁻¹	86.4 W h kg ⁻¹	3000	–	2016	[164]
Ppy	nt-G	0.15 A g ⁻¹	509 F g ⁻¹	32.7 kW kg ⁻¹	21.6 W h kg ⁻¹	13 000	75%	2016	[165]
Ni ₃ Se ₂	CF	2.0 A g ⁻¹	252 mA h g ⁻¹	0.7 kW kg ⁻¹	32.8 W h kg ⁻¹	5000	101%	2017	[166]
MnO ₂	CNP	–	–	3.7 mW cm ⁻¹	12 μW h cm ⁻¹	5000	102%	2017	[167]

Note: CC, carbon cloth; CF, conductive fabric; CM, carbon monolith; CNP, carbon nanotube paper; CNTs, carbon nanotubes; CNW, carbon nanowalls; Co-Ni-DH, Co-Ni double hydroxides; GR, graphene; GRT, graphene nanosheets-coated textiles; NA, nanotube arrays; NCA, nickel nanocone arrays; NF, Ni foam; nt-G, nanotubular graphene; PANI, polyaniline; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate); PPy, polypyrrole; SSM, stainless steel mesh.

Additionally, Yang and co-workers introduced the co-electrodeposition strategy to form a uniform MnO₂ and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) nanostructured composite for supercapacitor electrode. The fabricated electrode exhibits high areal capacitance (1670 mF cm⁻² at 0.5 mA cm⁻²), high areal mass (8.5 mg cm⁻²), excellent mechanical robustness, as well as a high throughput characteristic and great convenience even on a piece of stainless steel mesh current collector (**Figure 11**).^[19] This electrode was used as the positive electrode and the activated carbon film was used as the negative electrode. The as-prepared supercapacitor device was ultrathin (less than 200 μm), flexible and light-weight, with a high energy density (1.8 × 10⁻³ W h cm⁻³), a high-power density (0.38 W cm⁻³ at 3.62 × 10⁻⁴ W h cm⁻³) and excellent rate capability. Moreover, they reported a simple and efficient method to fabricate ultrathin and flexible supercapacitors, employing 3D nickel nanocone arrays (NCAs) as scaffold, and MnO₂ or graphene (GR) as active materials, which showed excellent mechanical flexibility and electrochemical stability (**Figure 12**).^[131] These flexible micro-supercapacitors as the power sources for wearable electronics and other miniaturized devices may meet a vast application, especially in the cases where the devices are required to

endure winding, folding, twisting, and even laminating. In general, electrostatic deposition technique is applicable to a large range of material species other than the reported MnO₂ and GR.

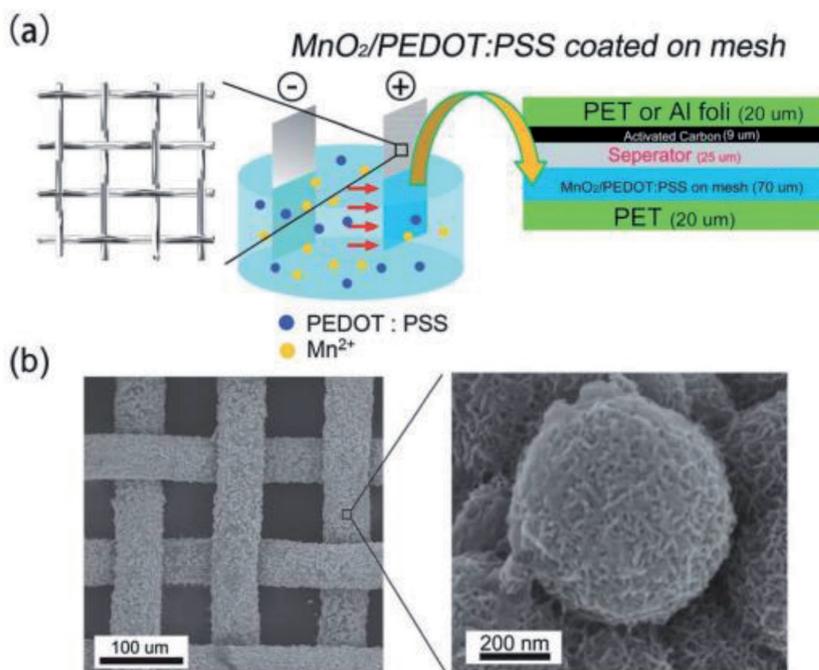


Figure 11. a) Schematic of the fabrication process of the MnO₂-PEDOT:PSS nanocomposite. b) SEM images of the MnO₂-PEDOT:PSS nanocomposite. Reproduced with permission.^[19] Copyright 2013, The Royal Society of Chemistry.

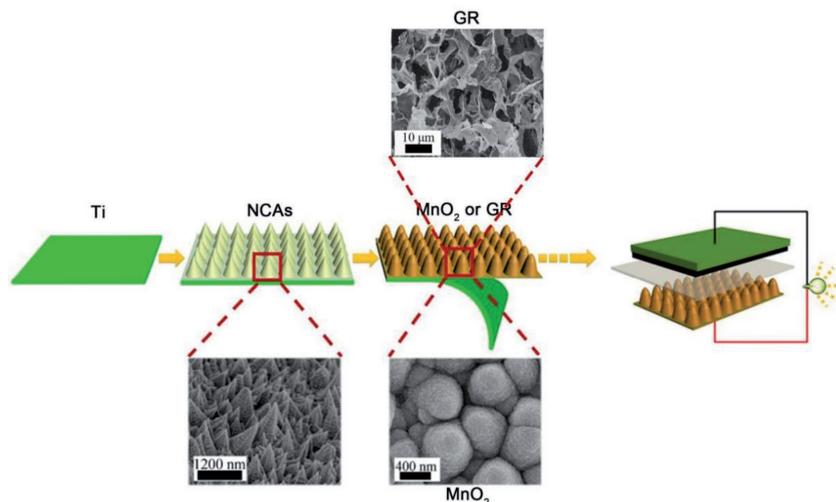


Figure 12. Schematic illustration of the fabrication process for the ultrathin supercapacitor based on MnO_2 or GR as active materials. Reproduced with permission.^[131] Copyright 2013, The Royal Society of Chemistry.

On the basis of electric field, electrostatic deposition-based techniques can enable chemical reactions on the surface of electrode materials directly and efficiently. Electrostatic deposition-based techniques as a kind of liquid phase deposition technique reveals remarkable characteristics in directly self-assembled nanostructure electrodes, and are suitable for uniform deposition of various complex substrates. Also, they are a distinctive tool to build ultrathin supercapacitors due to the uniform and controllable thickness. In order to meet the need of high energy density electronic products, some highly conductive substrate materials have been employed as scaffolds, and various electroactive materials have been explored as electrode materials. Relying on the exceptionally conductive and mechanical properties, the scaffold materials can support for the deposition of electroactive materials, which can not only increase the specific capacitance of active materials, but also relieve the cycle degradation problems caused by mechanical failure.^[168] Moreover, the electrode materials prepared by electrostatic deposition-based techniques do not involve either polymer binder or conductive additives, which can avoid decrement of electrical conductivity of the electrode materials, that is important for high-performance supercapacitors. Contemporarily, researches on high-performance supercapacitors tend to make the deposition of electroactive materials on those highly conductive scaffolds. Due to the strong cohesion between scaffold materials and electroactive materials, the electrodes may improve the ion migration rate and conductivity greatly. This makes electrostatic deposition-based techniques combined with the utilization of highly conductive scaffold substrates find vast applications in the future high-performance energy storage devices, such as hybrid electric vehicles, wireless sensor networks, etc.

3.3. Electrospinning-Based Techniques

Electrospinning-based techniques are another interesting application of electrostatic field, which are regarded as a simple,

versatile, and cost-effective method to fabricate highly porous, nanofibrous electrode structures as well as separator for supercapacitors. In 1914, electrospinning was first studied by Zeleny and co-workers; subsequently, Anton applied the first patent about electrospinning technique.^[169,170] Afterwards, electrospinning has been extensively used as a facile method for investigation of nanofibers and nanowires in energy-related applications. Besides the metallic spinneret and syringe pump, a typical electrospinning setup also consists of a specialized device supplying a high-voltage power, a grounded collector for preventing the electric shock and protecting the safety of equipment (**Figure 13**).^[171] The basic principle of electrospinning is using electrostatic force to draw charged threads from polymer solutions or polymer melts up to fibers with the diameter of several dozen of nanometers. Electrospinning-based techniques share characteristics

of both ESD and conventional solution dry spinning of fibers, and can be regarded as a special case of ESD. The biggest difference between ESD and electrospinning is the working medium. ESD employs Newtonian fluids with a low viscosity, while electrospinning utilizes non-Newtonian fluid with a high viscosity. The process of electrospinning-based techniques does not involve the use of coagulation chemistry or high temperature, which can produce solid threads from the stock solution. This makes the process particularly suitable for the production of fibers using high and complex molecules. Besides, electrospinning from molten precursors is also practiced, so as to ensure the final product without the existence of solvent.^[172] Currently, electrospinning has been broadly employed to continuously fabricate ultrafine fibers of polymers, metal-oxides and their composites with controllable composition and pore structure with the diameters ranging from micrometer to nanometer.^[173–175]

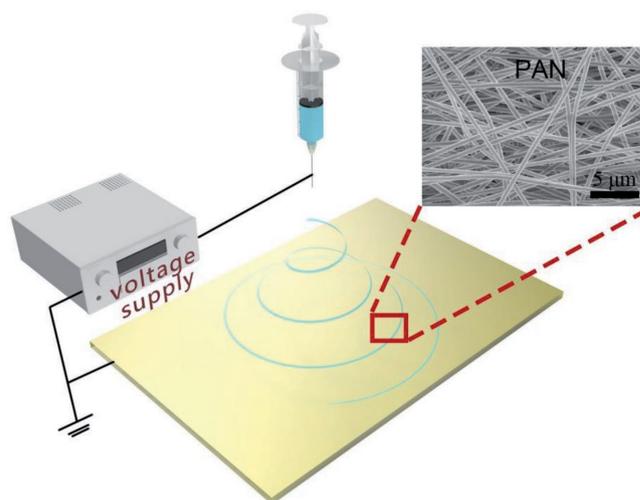


Figure 13. Schematic illustration of an electrospinning setup.

Table 3. The electrode materials prepared by electrospinning and its electrochemical performance.

Electrode materials	The precursor	Diameter [nm]	The specific surface area [m ² g ⁻¹]	Current density	Specific capacitance [F g ⁻¹]	Power density [kW kg ⁻¹]	Energy density [W h kg ⁻¹]	Cycling number	Capacity retention	Year published	Refs.
ACF	PBI	250	1220	1 mA cm ⁻²	202	–	–	–	–	2005	[177]
ACF	PAN/ZnCl ₂	100	550	–	140	–	–	–	–	2007	[178]
CNTs/CF	PAN	–	810	0.1 A g ⁻¹	310	–	–	1000	97%	2009	[179]
V ₂ O ₅	PVP/VAAC	300–500	10	5 mV s ⁻¹	190	1.8	78.0	–	–	2010	[180]
Fe ₃ O ₄ /CF	PAN	400–500	–	0.42 A g ⁻¹	135	–	–	1000	91%	2011	[181]
TiN/VN	–	300–660	169	2 mV s ⁻¹	248	–	–	500	88%	2011	[182]
CF/GNS	PAN/GNS/DMF	–	447	1 A g ⁻¹	197	–	–	1500	84%	2012	[183]
CF/MnO ₂	PAN/Fe(acac) ₂	200	102	2 mV s ⁻¹	311	57.7	80.2	1000	≈98%	2012	[184]
NiCo ₂ O ₄	PVP	89	37	1 A g ⁻¹	1647	0.2	38.5	3000	94%	2013	[185]
PANI	PAA	400	–	1 A g ⁻¹	601	–	–	500	62%	2013	[186]
CF	PAN	200–400	1600	1 A g ⁻¹	210	20.0	4.0	–	–	2013	[171]
Co ₃ O ₄	PVA	100–300	33	–	–	–	–	10 000	98%	2015	[187]
NPCNFs	PAN/PANI	–	410	0.5 A g ⁻¹	335	0.25	9.2	10000	86%	2016	[188]
CP	PAN	200	–	–	150	–	13.3	1000	–	2017	[189]
CF	ZIF-8/PAN	140	–	1 A g ⁻¹	332	–	–	5000	98.9%	2017	[190]

Note: acac, acetylacetonate; ACF, activated carbon nanofibers; CF, carbon nanofibers; CP, carbon paper; CNTs, carbon nanotubes; DMF, dimethylformamide; GNS, graphene nanosheet; NPCNFs, nitrogen-doped porous carbon nanofibers; PAN, poly(acrylonitrile); PANI, polyaniline; PBI, polybenzimidazol; PVA, poly(vinyl alcohol); PVP, polyvinyl pyrrolidone; VAAC, vanadyl acetylacetonate; ZIF-8: zeolitic imidazolate framework-8.

In brief, electrospinning is based on the electrostatic repulsion force supplied from electric field to make fluidic polymer droplets drop onto the tip of a spinneret. With the gradual increase of the electric field, the electrostatic repulsion inside the charged solution becomes larger than its surface tension when it reaches a critical value. After that, a charged jet of the solution will eject from the tip of the spinneret. Subsequently, the jet soon enters a bending instability stage with further stretching of the solution jet under the electrostatic forces as the solvent evaporates, then the solidified, continuous, ultrathin fibers can be collected on the substrate.^[156] The diameter of the nanofibers can be well controlled by several parameters, e.g., the applied voltage, solution viscosity, electrical conductivity, spinneret tip-to-collector distance, precursor concentration, and flow rate of the solution. The electrospun nanofibers present specific properties, including an extremely high surface area and pore volume, tunable porosity, low density, and exceptional mechanical strength.^[176] **Table 3** shows the recent research advance about electrospinning in the application of high-performance supercapacitors, which demonstrates the universality and reliability of electrospinning-based techniques for the preparation of various electrode materials.

To date, many efforts have been made to fabricate carbon nanofibers and nanotubes from electrospun precursors.^[179] For example, poly(acrylonitrile) (PAN)-based precursors with subsequent steam activation to fabricate nanofibers with low fiber diameter, high mat porosity, and freestanding nature, which exhibit high electrochemical performance for the fabrication of supercapacitor electrodes. PAN is often used as a precursor material due to its good spinnability in solution and relatively high carbon yield.^[191] Kim and Yang reported the electrospun carbon nanofiber web as an electrode for supercapacitors,

which PAN-based precursor could provide a high specific surface area and high porosity for the mobility of ions, resulting in the maximum specific capacitance of the as-prepared electrode.^[192] The prepared electrospun nanofibers exhibits free-standing nature and can be used as electrodes without any binder. Other precursors, such as polyimide (PI), polybenzimidazol (PBI), isotropic pitch fiber, and poly(amic acid) (PAA) have also been reported,^[177,186,193–195] and the electrochemical performance of the electrospun nanofiber-based supercapacitors is shown in **Table 3**.

This fabrication technique offers unique and flexible capabilities for the continuous fabrication of nanofibers and fabrics by virtue of its simple experimental setup, stable processing technology, and high reproducibility for controlling the composition.^[191,196,197] It takes relatively facile processes to fabricate nanofibers with high surface area and porosity, which can control the fiber morphology effectively. Electrospun nanofibers incorporated with the highly conductive active materials shall receive beneficial effects, and the composite electrodes may exert both high specific surface area and specific capacity. More importantly, the electrodes prepared by using electrospun nanofibers demonstrate excellent mechanical strength, that is propitious to fabricate stretchable, flexible, self-supporting supercapacitors for various rollable and wearable electronic devices, miniature equipment and so on. However, this technique still faces challenges in large-scale production, which currently limits its commercial developments. Nevertheless, electrospinning as an indispensable means of external electric field has been showing capability of nanofiber productions with excellent uniformity. Meanwhile it can give rise to more complex architectures and novel composite materials via co-electrospinning, which may play a vital role for the improving

electrochemical performance of supercapacitors as well as an irreplaceable benchmarking in future technical improvement.

4. Electrode Fabrication Techniques Based on Magnetic Field

The magnetism of materials originates from the movement of the electrons in the atom, which generate an electromagnetic vortex of Ethernet via their spin and the orbital motion around atomic nucleus.^[198] Basically, there are two kinds of magnet, including permanent magnet and soft magnet, which can generate magnetic field. Permanent magnet can maintain its magnetism for a long time or even forever, e.g., NdFeB magnet, AlNiCo magnet, SmCo magnet, and ferrite permanent magnets. Magnetic field is referred to the magnetic effect of electric currents and magnetic materials, which can be produced by moving electric charges and the intrinsic magnetic moments of elementary particles, associated with their fundamental quantum property.^[199] When exposing to a magnetic field, magnetic material will be magnetized to arise many tiny magnetic dipoles, so as to make them in directional moving. As magnetic field is a vector field, any given points in the magnetic field can be specified by their directional and magnitude information.^[199,200]

When placed near to permanent magnets, ferromagnetic materials such as iron, cobalt, and nickel can be aligned with their magnetic moments. Magnetic field-based electrode fabrication techniques trigger interesting performance characteristics with the merits of simplicity, environmental friendliness, low-cost, and controllability, etc, which have been widely used in EES field. To date, there are two main applications relying on magnetic field for supercapacitors. The first one is using magnetic field to drive nanostructured materials self-assembly,^[20,201–205] and the second one is introducing magnetic field into the electrochemical testing process to enhance capacitive performance.^[206–210] Both of these two aspects have been investigated extensively, and the details are as following.

Recently, there have been more attentions on the rational designs of electrodes with 3D functional hierarchical structures, which can not only improve the charge and mass transport abilities but also help to release the stress caused by electrochemical cycling.^[20] Transition metals and their oxides have been considered superior active materials than conventional carbon materials.^[211] Different from the conventional template-growth methods and hydrothermal methods, employing magnetic field does not involve complex preparation steps and removal of templates. It is introduced as an effective tool to control chemical reactions and materials syntheses owing to its influence on the electrical conductivity, crystal structure, and morphology of various materials.^[212–216] For instance, Kawamori et al. have investigated external magnetic field-based techniques, who reported about the directional movement of nickel nanoparticles to form unique electrode morphology relying on the ferromagnetic property of nickel.^[201,202] Kawamori et al. successfully synthesized nickel nanowires with diameter ranging from 100 to 370 nm and several dozen microns in length via electroless deposition when exposed to a magnetic field.^[201] In addition, they demonstrated that nickel nanoparticles could be connected

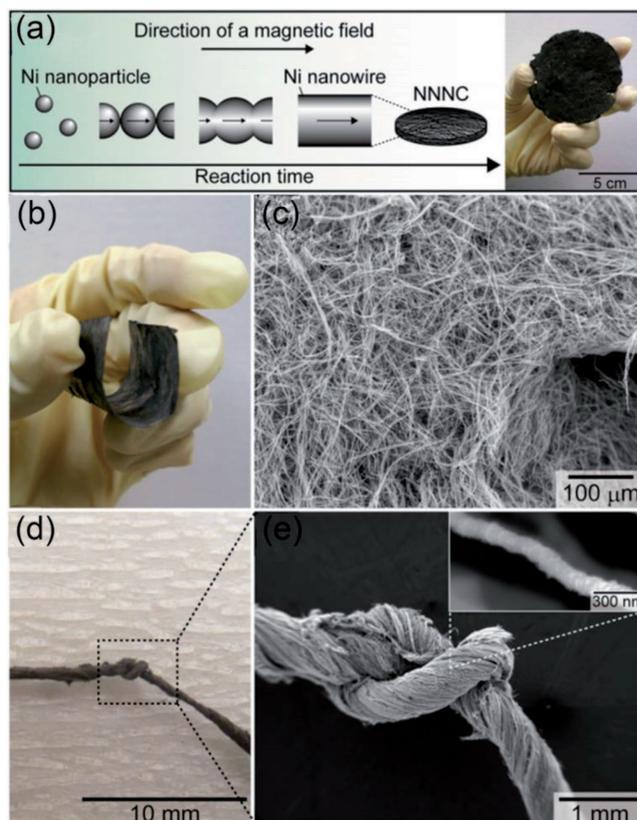


Figure 14. a) Schematic illustration of the formation process of the NNNC under a magnetic field. b) Photographic and c) SEM images of the sheet-like NNNC. d) Photographic and e) SEM images of the twisted and tied nickel nanowires. Reproduced with permission.^[202] Copyright 2014, American Chemical Society.

together and eventually form nanowires because of shape magnetic anisotropy, and then the nickel nanowires entangled into a self-assembled nonwoven cloth, called as a NiO-covered nickel nanowire nonwoven cloth (NNNC) (Figure 14).^[202] Under external magnetic field, the metal nanowire nonwoven cloth (MNNC) demonstrates both flexibility of the metal sheet and large specific surface area of the nanowires, which is an excellent motif of electrode framework for the deposition and coating of active materials. In consequence, MNNC with a unique porous structure can not only be conducive to electron and ion transportation, but also meet superior electrochemical performance by cladding other electroactive materials. Recently, Yang and co-workers prepared, for the first time, a vertically aligned Ni nanowire array (NNA) nanostructure with diameter of each nanowire ranging from 120 to 170 nm and length up to 1 mm under magnetic field (NdFeB magnet).^[20] Using NNA as the electrode scaffold, MnO₂ and polypyrrole (PPy) were both electrodeposited on its surface regarding as the cathode and the anode, respectively, and then assembled into an aqueous asymmetric microsupercapacitor (Figure 15). This microsupercapacitor with superior energy density, outstanding cycle stability and excellent mechanical flexibility can be used in a wide range of promising energy storage applications.^[215–217] In addition, Liu et al. demonstrated that the 1D wire-like NiO/Co₃O₄ composites could be fabricated by a simple magnetic field-assisted

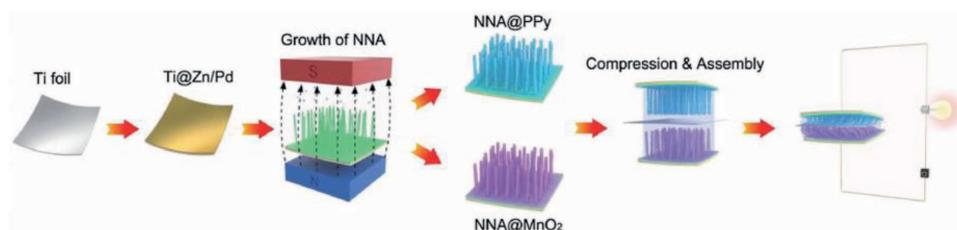


Figure 15. Schematic illustration of the fabrication process of an asymmetric supercapacitor based on NNA under NdFeB magnet. Reproduced with permission.^[20] Copyright 2016, WILEY-VCH.

hydrothermal method, which indicated that these magnetic Ni/Co nanoparticles were assembled into a chainlike structure along the direction of magnetic force line under the magnetic interaction, thus forming a 1D wire-like Ni/Co alloys.^[204] Zhu et al. reported that a nanostructured MnO₂ film could be deposited onto nickel foams by a hydrothermal synthesis route under a low magnetic field, which exhibited a specific capacitance of 493.0 F g⁻¹ at 2.0 A g⁻¹ and a retention ratio of 95.6% over 1000 cycles.^[205] A probable formation mechanism for the nanostructured MnO₂ was proposed in which magnetic field acted as a force field with strong vibration and destruction abilities. This could induce the initially formed tiny nuclei turn into lots of pieces, and interferes the nucleation rate and the subsequent growth and aggregation processes. Based on the above effects, the morphological and electrochemical performance of MnO₂ electrode would be greatly subjected by the magnetic field. Therefore, a moderate magnetic field shall be an economic and effective tool in the synthesis of MnO₂ electrodes for high-performance supercapacitors. All of these results indicate that a magnetic field strongly affects the morphology of metal-based electrode materials, and subsequently improves the capacitance performance of the supercapacitors.

Another appealing application is that **magnetic field can enhance the capacitive performance** during the electrochemical testing process. The schematic setup of the electrochemical cell tested in a magnetic field is shown in **Figure 16**. Zhu et al. reported that the presence of an external magnetic field was capable to induce significant enhancement on the capacitance in both graphene and magnetic graphene nanocomposites

(MGNCs) electrodes. The specific capacitance of graphene was increased by 67.1% and 26.8% at the scan rates of 2 and 10 mV s⁻¹, respectively. Even larger enhancements of 154.6% and 98.2% were observed in MGNCs at the same scan rates of 2 and 10 mV s⁻¹, respectively.^[207] **This significant capacitance enhancement is attributed to the improved energy state of the electrons in magnetic field, and then the energy state of electrons would increase the electron transportation efficiency at the electrolyte-electrode interfacial area during electrochemical process.**^[207,209] Additionally, Zhu et al. also reported magnetic carbon-metal (iron, cobalt, or nickel) oxides microtubular nanocomposite fabrics as flexible electrodes, which could significantly influence the specific capacitances by applying a weak magnetic field.^[209] The corresponding mechanism can be interpreted by the synergistic effect of three internal resistances, i.e., solution resistance in electrolyte, charge transfer resistance at electrode/electrolyte interface, and leakage resistance in electric double-layer region. The applied magnetic field plays a critical role in restricting the interfacial relaxation process, which is able to change the solution resistance due to the magneto-hydrodynamic phenomenon, as well as the electrode resistance (directly corresponding to charge transfer resistance) by the magnetoresistance behavior; and therefore enhancing the electrode capacitance. However, the introduction of external magnetic field can also reduce the specific capacitance of supercapacitors. Wei et al. found that the magnetic field was unfavorable for the electrochemical performance of the silica-doped PANI nanocomposites, which could also be explained by the magnetoresistance phenomenon.^[206] When exposed to a

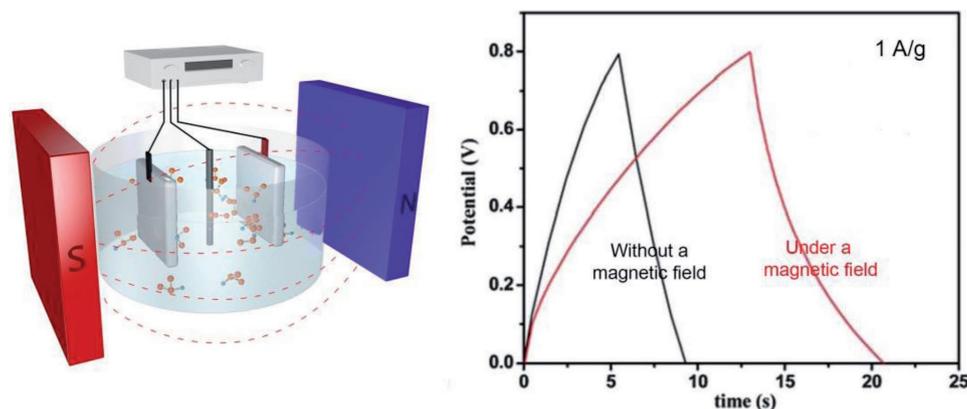


Figure 16. The schematic setup of the electrochemical cell tested in a magnetic field. Reproduced with permission.^[207] Copyright 2013, The Royal Society of Chemistry.

magnetic field, the transport path length of the charge carriers increases and the number of the charge carriers along with the electric field direction becomes lower due to the Lorentz force, resulting in the increment of resistance.^[218–220] In consequence, the introduction of magnetic field in the electrochemical testing process can change the capacitive performance of supercapacitors, which is dependent on the magnetohydrodynamic phenomenon. Interestingly, these findings present a potential prospect that the capacitance of traditional electrochemical capacitors can be enhanced dramatically via simply applying an external magnetic field without materials replacement and structural modification, which discloses a great impact on the electrochemical energy storage field.

In short, electrode fabrication techniques based on magnetic field are facile and available methods to render high-performance supercapacitor electrode materials. Magnetic field not only aligns magnetic nanostructures but also has great potential to enhance the capacitive performance of supercapacitors. Besides the magnetic materials, some nonmagnetic materials such as carbon-based materials may also be induced to self-assemble by coating the magnetic responsive media like ferrofluid on their surface, which can widely broaden the application of magnetic field-based techniques. Hence, magnetic field-based techniques can activate a great interest for the fabrication of compressible and freestanding thin-film supercapacitors, which reveals a wide range of applications.

5. Summary and Outlook

In order to keep up with the pace of future portable and wearable electronics technologies, the technical innovation of nanostructured supercapacitor electrodes becomes more important than ever. The rising electrode fabrication technologies including electrostatic field, magnetic field, and dynamic electromagnetic field-based techniques, are becoming more powerful tools for constructing complicated, hierarchical, and well-ordered nanostructured electrodes. These emerging techniques provide numerous advantages such as green, simple, and mild reaction conditions, and high efficiency due to its unique forms and functional mechanisms. All these features are important to render high-performance electrode at micro-nanoscale, which can significantly contribute to the development of novel supercapacitor electrode fabrication technologies.

Electrode fabrication techniques based on electromagnetic field can be divided into microwave reaction, lights, laser, high energy ray-, and particle-based techniques. Typically, microwave reaction-based techniques have been extensively utilized to render porosity of various electrode materials, which exhibit high surface areas, abundant reaction sites, and highly dispersed channels. On the other hand, IR light, visible light, and UV light can be applied to prepare carbon nanomaterials for supercapacitor electrodes, displaying an enormous exploration potential applications. In response to the large-scale electrode materials processing and miniaturized electronic device productions, laser-assisted fabrication techniques have drawn attention to a great extent by the virtues of its high efficiency and low cost, which can conveniently carry out precision machining.

Besides, high energy ray and particle-based techniques provide an efficient method for the modification and functionalization of electrode materials with high specific energy. But the risks to human beings shall be carefully considered and evaluated for large-scale industrial production. It is noteworthy that combining dynamic electromagnetic field-based techniques with different kinds of photomasks or patterns can lead to the fabrication of ultrathin, lightweight, and miniature supercapacitors, which reveal great potential in modern technological applications.

The wet process electrostatic field-based techniques are also utilized for the fabrication of supercapacitor electrodes for the applications of various flexible, wearable, and portable electronics. For industrial point, electrostatic deposition-based techniques, are a promising direction for depositing active materials onto highly conductive scaffold substrates, exerting the advantages of composite structure as much as possible for high-performance supercapacitors. ESD is among one of the electrostatic field-based technique, which can induce some low-dimensional nanomaterials for self-assembly due to solvent evaporation and thickness-controllable electrode. Especially, ESD techniques can not only eliminate the use of conductive agents and binders, but also minimize the aggregation effect of the sprayed matters. ESD-based techniques hold a great promise in the preparation of various precursor electrode materials in thin-film supercapacitors and microsupercapacitors. As for electrospinning-based techniques, they are a relatively facile process for the fabrication of nanofibers with high surface area and porosity, which can control over the fiber morphology effectively. Even though electrospinning-based techniques are still quite expensive for large-scale production, constructing complex architectures, and novel composite materials as supercapacitor electrodes via coelectrospinning-based techniques are a bright development trend for commercial electronic fields.

Electrode fabrication techniques based on magnetic field consist of two categories, one is driving nanostructured materials for assembly and alignment under a magnetic field, the other one is introducing magnetic field into the electrochemical testing process. Both of them are beneficial for the fabrication of high-performance supercapacitors. But in contrast, the former one emerges an unprecedented potential to fabricate novel porous conductive scaffolds, which is advantageous for the deposition of various active materials, supporting for the preparation of versatile supercapacitors with outstanding electrochemical performances. Magnetic field-based techniques are more likely used to develop high mass loading supercapacitors for the application prospects of hybrid electrical vehicles, mobile phones, laptops, and digital cameras, etc.

In summary, this review article lists the recent progresses and advancement utilizing various electromagnetic techniques for the design and engineering of nanostructured electrodes on the application of high-performance supercapacitors. We aim to elucidate the huge advantages and prospects of electromagnetic field, electrostatic field, and magnetic field-based techniques in the fabrication of supercapacitor electrodes. All aspects of the data demonstrate that electromagnetic techniques create boundless imagination and enlightenment for the development of versatile supercapacitors.

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