

Flexible Graphene-, Graphene-Oxide-, and Carbon-Nanotube-Based Supercapacitors and Batteries

Runzhi Zhang, Anthony Palumbo, Jae Chul Kim, Junjun Ding, and Eui-Hyeok Yang*

Flexible energy-storage devices increasingly attract attention owing to their advantages of providing lightweight, portable, wearable, or implantable capabilities. Many efforts are made to explore the structures and fabrication processes of flexible energy-storage devices for commercialization. Here, the most recent advances in flexible energy-storage devices based on graphene, graphene oxide (GO), and carbon nanotubes (CNTs), are described, including flexible supercapacitors and batteries. First, properties, synthesis methods, and possible applications of those carbon-based materials are described. Then, the development of carbon-nanotube-based flexible supercapacitors, graphene/graphene-oxide-based flexible supercapacitors, and graphene- and carbon-nanotube-based flexible battery electrodes are discussed. Finally, the future trends and perspectives in the development of flexible energy-storage devices are highlighted.

systems. The key challenge of flexible energy-storage devices is to achieve the device performance that is superior or comparable to the existing rigid devices, while under bending or stretching. Though there is significant potential for the application of flexible energy-storage devices, the operating performance still needs to be improved to meet the harsh requirements of industry. In order to improve the performance of the flexible energy-storage devices, efforts are concentrated to optimize devices with appropriate materials that enable the fabrication of flexible energy-storage devices with desirable electrochemical properties. Several wearable and printable electronics devices are demonstrated.

1. Introduction

Flexible systems show unique promising advantages, such as flexibility, stretchability, lightweight, and mechanical conformability.^[1] For instance, flexible energy-storage devices are potential backups for healthcare and monitoring applications, flexible displays, wearable applications, and military applications.^[1–3] Currently, energy-storage systems are classified into four types as shown in **Figure 1**: mechanical, chemical, electrical, and electrochemical.^[4] These energy-storage and conversion devices, such as supercapacitors, batteries, fuel cells, and solar cells are usually comprised of rigid and/or bulky components, and therefore too heavy to meet the requirements for flexible and portable electronics. Therefore, there is a trend to develop energy-storage devices for the aforementioned flexible

Proposed strategies include the production of hybrid materials using carbon-based materials with active materials,^[5] control of the micro/nano-structure,^[6] optimization of the particle size,^[7] and combination of super flexible materials.^[8] Despite this progress, there are still many challenges in the development of flexible energy-storage devices, given that flexible electronics is in the early stages of development and no perfect evaluation standards exist to characterize the corresponding flexible devices.^[9]


Many electrode materials are used for the fabrication of flexible supercapacitors and batteries. Graphene- and carbon nanotube (CNT)-based materials attract much attention as potential energy-storage platforms due to their inherent mechanical flexibilities.^[10,11] Conducting polymers, such as polypyrrole (PPy) and polyaniline (PANI), are particularly interesting electrode materials since they show relatively high capacitance toward supercapacitor and battery applications.^[2,12,13] Typically, these polymer-based supercapacitors and batteries show poor cycling stabilities due to the swelling during cycles of charge and discharge, high self-discharge rates, and mass transport limitations with thick polymer layers.^[14] Metal oxides are used as low-cost electrode materials for supercapacitors with high specific capacitance, but they show relatively marginal electrical conductivity (electrical conductivity as high as $\approx 200 \text{ S cm}^{-1}$).^[9,15] Carbon-based materials possess very large surface areas, excellent electrical conductivity, and mechanical flexibility.^[16,17] The combination of conducting polymers and various types of carbon materials are also used as electrode materials to overcome limitations in the cycling stability.^[18–21]

Here, we focus on describing the recent development of graphene-, graphene oxide (GO)-, and CNT-based flexible supercapacitors and batteries. In the first part, we review the

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properties, syntheses, and applications of graphene, GO, and CNTs. In the second part, we review the latest examples of flexible supercapacitors based on CNTs, graphene, and GO. The challenges and opportunities of the fabrication are also discussed. In the following part, we briefly review how these materials are used in batteries as a main energy-storage component. Finally, we provide a summary and give our perspectives for the continued development of flexible energy-storage.

2. Properties, Syntheses, and Applications of Graphene, Graphene Oxide, and Carbon Nanotubes

2.1. Graphene

2.1.1. Properties

In 2004, Novoselov et al. successfully obtained graphene, a monolayer of carbon atoms that has a honeycomb lattice, via mechanical exfoliation from graphite.^[22] Since its discovery, graphene has been extensively explored across virtually all areas of science and engineering. Graphene shows superior mechanical, thermal, and electrical properties. For example, the reported tensile strength and Young's modulus, and thermal conductivity of graphene are >100 GPa, ≈ 1 TPa,^[23] and $\approx 5 \times 10^3$ W mK⁻¹,^[24] respectively. The electrical conductivity is estimated as high as 1×10^5 S cm⁻¹, suitable for diverse electronic applications.^[25] In addition, graphene has a high specific surface area of ≈ 2600 m² g⁻¹,^[26] which is desirable for energy-storage applications such as supercapacitors and batteries.

2.1.2. Synthesis

Graphene is obtained using various synthesis methods, including reduction of GO, epitaxial growth, and chemical vapor deposition (CVD).^[27] For instance, graphene is grown epitaxially by thermal desorption of carbon from SiC at 1000 °C in ultra-high vacuum, as confirmed by scanning tunneling microscope.^[28] CVD is also employed to produce graphene using transition metal substrates.^[29] Carbon atoms saturated on transition metals at high temperature under hydrocarbon gas flow precipitate as graphene upon cooling. Depending on substrate selection, few-layer graphene (on a Ni substrate) or single-layer graphene (on a Cu substrate) is obtained.^[30,31]

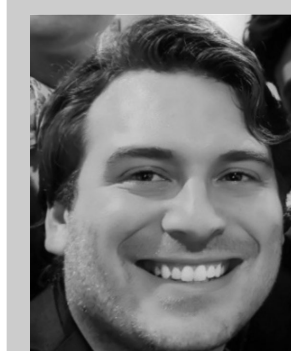
2.2. Graphene Oxide

2.2.1. Properties

GO is a layered graphene sheet with hydrophilic oxygen functional groups on their basal planes and edges. GO is obtained by exfoliating graphite oxide into layered sheets through sonication or mechanical shearing.^[32] During the graphite oxidation and exfoliation process, the graphene-based lattice bears various oxygen-containing groups, including epoxy and hydroxyl



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devices.



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groups.^[33] The oxygen functional groups on GO surfaces and edges differentiate GO from pristine graphene with fascinating properties.^[34,35] When GOs are functionalized by epoxide and/or hydroxyl groups that are hydrophilic, water molecules are intercalated between their layers, leading to exfoliation upon additional mechanical energy.^[36]

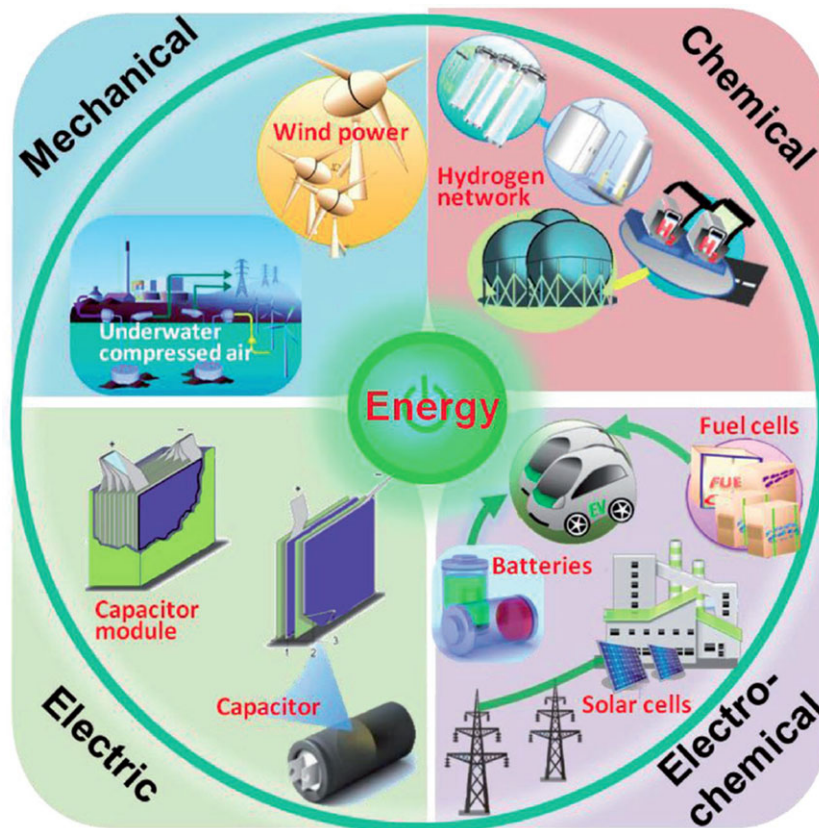


Figure 1. Classification of different types of energy-storage technologies for stationary applications. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (<https://creativecommons.org/licenses/by/4.0/>).^[4] Copyright 2017, The Authors, published by Wiley-VCH.

The functional groups added to GO surfaces and edges provide effective anchoring sites to other atoms, molecules, etc. The functional groups not only enable various molecular and bio-sensing applications but also provide tunable electronic properties. Unlike pristine graphene, GO generally possesses a high sheet resistance of around $1000 \Omega \text{ sq}^{-1}$ or higher due to the large portion of sp^3 hybridized carbon atoms bonded with oxygen functional groups.^[35] The sheet resistance decreases by reducing the GO into reduced graphene oxide (rGO), transforming the insulating GO into a conductive graphene-like sheet. By controlling the oxygen functional groups, mainly epoxy and hydroxyl groups, rGO is transformed into a semiconductor with a tunable bandgap.^[37–40] By a reduction process, the conductivity of GO is substantially increased via restoration of disrupted conjugated sp^2 bonds responsible for graphene's excellent conductivity. A schematic illustration of possible ways for the preparation of graphene, GO, and rGO is shown in **Figure 2**.^[41] Depending on the reduction process involved, different forms of graphene are prepared (i.e., chemically, electrochemically, and thermally reduced GO, abbreviated as CRGO, ERGO, and TRGO, respectively).

The oxygen functional groups on GO also make a significant contribution to its hydrophilicity. GO is dissolved in water due to the hydrogen attracted oxygen functional groups. Its hydrophilic property makes it possible to prepare evenly mixed solutions with other water-soluble organic compounds, such as polyvinyl alcohol (PVA). Exhibiting good dispersion in polar water, ethylene

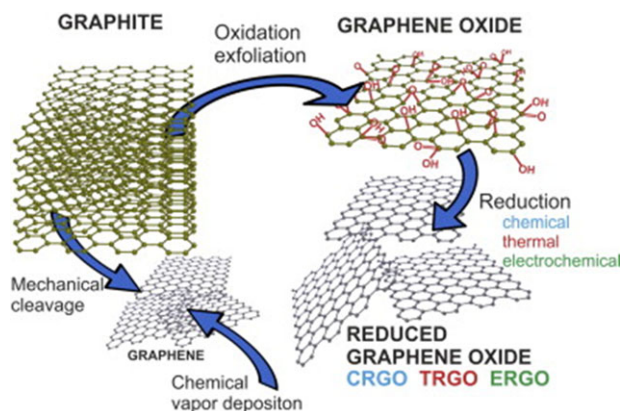


Figure 2. A schematic illustration of possible ways for preparation of graphene, GO, and rGO. Reproduced with permission.^[41] Copyright 2014, Elsevier Ltd.

glycol, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and tetrahydrofuran (THF) solvents also exhibit good dispersion and long-term stability with GO sheets. This enables solution-based mixing, which is effective to produce an even mixture for fabricating composites. Combining GO and other materials including ceramics and polymers, the GO composites are designed and fabricated to increase material properties.^[42–45] GO is

a unique amphiphile with negatively charged hydrophilic edges and hydrophobic basal planes; the arrangement enables GO to selectively interact with certain surfactants, which are capable of tuning the amphiphilicity of GO and controlling the assembly of rGO.^[46]

The optical and mechanical properties of GO are continuously changed by varying the film thickness and reduction degrees. GO water solution is usually dark brown to light yellow, based on the concentration of GO. The rGO thin film, however, is semi-transparent when the thickness is less than 30 nm. The mechanical properties of GO vary widely depending on the coverage of oxygen functional groups and thickness.^[47] The Young's modulus and strength of GO sheets are reported to be 6–42 GPa and 76–293 MPa, respectively.^[48–50]

2.2.2. Synthesis

GO is synthesized by chemical or mechanical exfoliation of chemically oxidized pristine graphite. The most common approach to graphite exfoliation is the use of strong oxidizing agents to yield GO.^[51] Potassium perchlorate and concentrated nitric acid mixture are used to oxidize graphite.^[52] A further improved method uses concentrated sulfuric acid, nitric acid, and potassium perchlorate to oxidize graphite into GO.^[53] This process enables the production of highly oxidized graphite at a laboratory scale. A method to prepare GO with concentrated sulfuric acid, sodium nitrate, and potassium permanganate continues to be commonly used today, known as Hummers' method.^[54] However, since this process generates toxic gases NO₂, N₂O₄, and/or ClO₂, a mixture of concentrated sulfuric acid and phosphoric acid with a volume ratio of 9:1 is used as a mixed acid, and potassium permanganate is used as a strong oxidant.^[51] In the aforementioned methods, graphite is oxidized, and the interlayer distance of GO increases from 0.34 nm to 0.8–1.0 nm because of the intercalation of oxygen functional groups.^[55,56] The van der Waals forces between adjacent graphene layers decrease, which benefits the exfoliation of GO sheets via chemical or mechanical exfoliation.^[57]

2.3. Carbon Nanotubes

2.3.1. Properties

Single wall CNTs (SWCNTs) and multiwall CNTs (MWCNTs) are widely used for energy-storage devices, owing to their excellent electrical, thermal, and mechanical properties. The structure of the types of CNTs determine their electrical properties, characterized by the chiral vector, $C_h = na_1 + ma_2$, where a_1 and a_2 are the basis vectors separated by 60°, and n and m are two positive integers; the three classes of CNTs are armchair ($n = m$), chiral ($0 < m < n$), and zigzag ($m = 0, n > 0$).^[58] The chiral vector of CNTs determine their electrical conductivity as either metallic or semiconducting. CNT is classified as metallic if this vector integer difference (e.g., $n - m$) is a multiple of three; otherwise, the CNT is semiconducting.^[59] Whether CNTs are metallic or semiconducting, their electrical properties are comparable to the best state-of-

the-art metallic and semiconducting materials. Strong carbon-carbon bonds of the “rolled” hexagonal carbon sheet that comprises CNT enable electrical conductivities up to 400 000 S cm⁻¹ and electrical mobilities on the order of 100 000 cm² V⁻¹ s⁻¹.^[60] A highly conductive network is formed from the combined high conductivity of individual nanotubes, whereas the charge carrier transport is limited by the large inter tube electrical resistance caused by the intrinsic charge barriers at tube-tube junctions.^[61] For perspective, nanotube film conductivity is reported up to 6000 S cm⁻¹, which is three orders of magnitude lower than the conductivity of a single nanotube.^[62]

Mechanical properties of CNTs make CNTs promising material candidates for flexible electronic devices. Mechanical characterizations of CNTs confirm that CNTs possess remarkable mechanical properties.^[63,64] CNTs have notoriously high Young's moduli (twice as high as SiC rods and orders of magnitudes higher than steel), in addition to remarkable flexibility in bending,^[65] twisting,^[66] kinking,^[67] and even buckling^[68] without damaging the nanotube. Notably, multiwall nanotubes laterally bent on a substrate via AFM probe until they twist over themselves show no sign of observable failure;^[69] furthermore, it is possible to make the tubes reversibly recover their original configuration, thus providing visible proof of their resilience, toughness, and flexibility.^[69] CNTs also have outstanding electrical, thermal, and optical properties,^[58,70,71] and properties of SWCNTs and MWCNTs vary significantly, as shown in **Table 1**.

2.3.2. Synthesis

The techniques for synthesizing CNTs are categorized into three methods: arc-discharge,^[92] laser ablation,^[93] and chemical vapor deposition (CVD).^[94] These procedures mainly involve gas phase processes, and the schematic illustration is shown in **Figure 3**. CNTs are synthesized from the electric-arc discharge technique as shown in **Figure 3a**.^[95] Two graphene rods are used as the anode and cathode. Under a helium atmosphere, a voltage and high temperature (over 1700 °C) are applied, and a build-up consisting of an outside shell of fused material and a softer fibrous core containing nanotubes and other carbon particles is formed.^[95] Laser ablation technique uses a laser to vaporize a graphene target, held in a controlled atmosphere at high temperatures near 1200 °C.^[96] High-temperature CNT synthesis techniques, such as arc discharge or laser ablation, precede low-temperature techniques such as low-temperature CVD (<800 °C), which is currently widely used with more precise control of the nanotube length, diameter, and density. CVD growth of CNTs also has the advantage of large-scale production and potential vertically aligned CNT growth.^[97] Many parameters influence the CNTs' synthesis, such as catalysts (Fe, Ni, and Co),^[98] growth temperature,^[99] and concentration of gas.^[100]

2.3.3. Fabrication of CNT-Based Flexible Electrodes

The unique properties of CNTs enable applications encompassing a multitude of fields and disciplines, including light emitters,^[103] composite materials for aerospace applications,^[104]

Table 1. The major properties of single wall CNTs and multiwall CNTs.

		SWCNTs	MWCNTs	Refs.
Physical properties	Diameter	0.7–3 nm	10–200 nm	[72,73]
	Carbon bond length	1.42 Å	1.42 Å	[74,75]
Mechanical properties	Elastic modulus	1 TPa	1.28 TPa	[76]
	Maximum tensile strength	≈100 GPa	≈100 GPa	[70]
	Yield strain	5–6%	12%	[77]
	Electrical conductivity	Metallic: 10^6 – 10^7 S m ⁻¹ Semiconducting: 10^{-2} – 10^2 S m ⁻¹	1.5 – 5×10^2 S m ⁻¹	[78–80]
Electrical properties	Resistivity (ballistic conditions)	10^{-6} Ω cm	3×10^{-5} Ω cm	[79,81–84]
	Emission current	4 μA	1.2 μA	[85]
	Maximum switching voltage (V_{sw})	800 V	1100 V	[85]
	Threshold field	2–3 V μm ⁻¹ (10 mA cm ⁻² current density)	3–5 V μm ⁻¹ (10 mA cm ⁻² current density)	[86]
	Thermal properties	Thermal conductivity	>3000 W m ⁻¹ K ⁻¹	>3000 W m ⁻¹ K ⁻¹
Relaxation time		≈10–11 s	≈1 s	[89,90]
Phonon mean free path		≈100 nm	≈20 nm	[78,89]
Optical properties	Transmittance	<90%	<65%	[62,91]
	Fundamental gap	Metallic: 0 eV Semiconducting: ≈0.5 eV	>1 eV	[71,89]

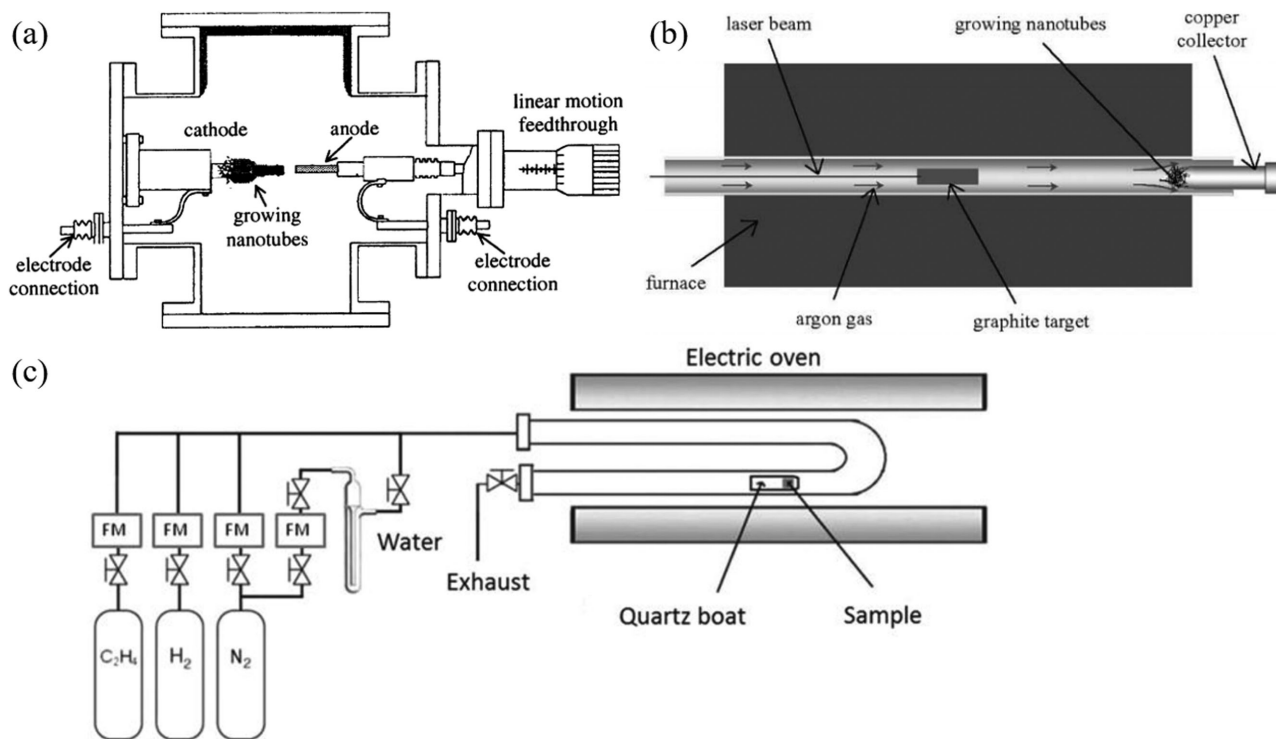


Figure 3. Schematic illustration of CNT synthesis techniques. a) Arc-discharge technique. b) Laser ablation process. c) Catalytic chemical vapor deposition technique. a) Reproduced with permission.^[101] Copyright 1996, AIP Publishing. b) Reproduced with permission.^[102] Copyright 2001, Elsevier Science Ltd. c) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>).^[100] Copyright 2017, The Authors, published by Springer Nature.

absorber coatings for thermal detectors,^[105] biomedical devices,^[106] energy-storage devices,^[107] electronic devices,^[108] and strength enhancing filler materials.^[109]

Owing to their advantageous mechanical and electrical properties, CNTs are promising materials for flexible electrodes, coinciding with the increasing demand of wearable and flexible electronic devices, which necessitates flexible electrodes. For the fabrication of CNT-based flexible electrodes, CNTs are usually deposited or embedded onto flexible or stretchable substrates such as polyethylene terephthalate (PET), polycarbonate (PC), or polydimethylsiloxane (PDMS).^[80,104,108,110–114] Furthermore, aligned CNT films are drawn from vertically grown CNT forests using the dry-drawing technique.^[115] Aligned CNTs result in a facile and low-cost process, in which one isolates CNT films and stacks them on a substrate for further processing, as shown in **Figure 4**. Cross-stacking of several layers of super-aligned CNT films enables a conductive and nanoporous network, exhibiting high mechanical strength, high surface area, and high transmittance of light.^[116] Wavy micro/nanostructures or open meshes facilitate mechanical deformations at large applied strains.^[117] CNT-based flexible electrodes demonstrate flexibility of 100% or greater,^[111,118–122] limited only by the cohesive fracture of elastomeric substrates. Stretchable CNT films embedded in PDMS achieve a stretching strain of 280%.^[123] 3M VHB 4905 substrates for CNT-based films enable a strain of 700%.^[124] The resistance of CNT on flexible substrates changes as a function of the strain;^[112,122,123,125] conducting spray-deposited films of SWCNTs on PDMS substrate demonstrate a conductivity of 2200 S cm^{-1} , and the film accommodates strains of up to 150%.^[126] The evolution of the resistance change during stages of applied strain and relaxation is shown in **Figure 5**.

3. Flexible Supercapacitors

3.1. Graphene/GO-Based Flexible Supercapacitors

Flexible electronics are leading the next revolution in electronics, including various research efforts on flexible electronics focused on flexible displays, electronic skins, epidermal sensors, and wearable medical devices.^[127–135] Despite the rapid development of these flexible functional devices, the bottleneck that hinders flexible electronics from practical use is the lack of flexible power sources. Current power sources such as lithium-ion batteries and energy harvesters are still quite heavy and bulky to be integrated into a flexible electronic system. Flexible energy-storage devices such as deformable supercapacitors are thus developed as light, thin, flexible power sources for flexible electronic systems. The supercapacitors are required to exhibit ultrahigh capacitance, high power density, and long lifetime. The key challenge for flexible supercapacitors is to deliver stable performance under continuous mechanical deformations, such as bending, twisting, and stretching.^[129,136,137]

Supercapacitors are classified into two main categories based on the energy-storage mechanism: electric double layer capacitors (EDLCs) and pseudocapacitors.^[138] For EDLCs, the capacitance is proportional to the specific surface area of electrodes. Graphene and GO are well known for their ultra-high surface area (up to $2675 \text{ m}^2 \text{ g}^{-1}$), tunable electrical conductivity, strong

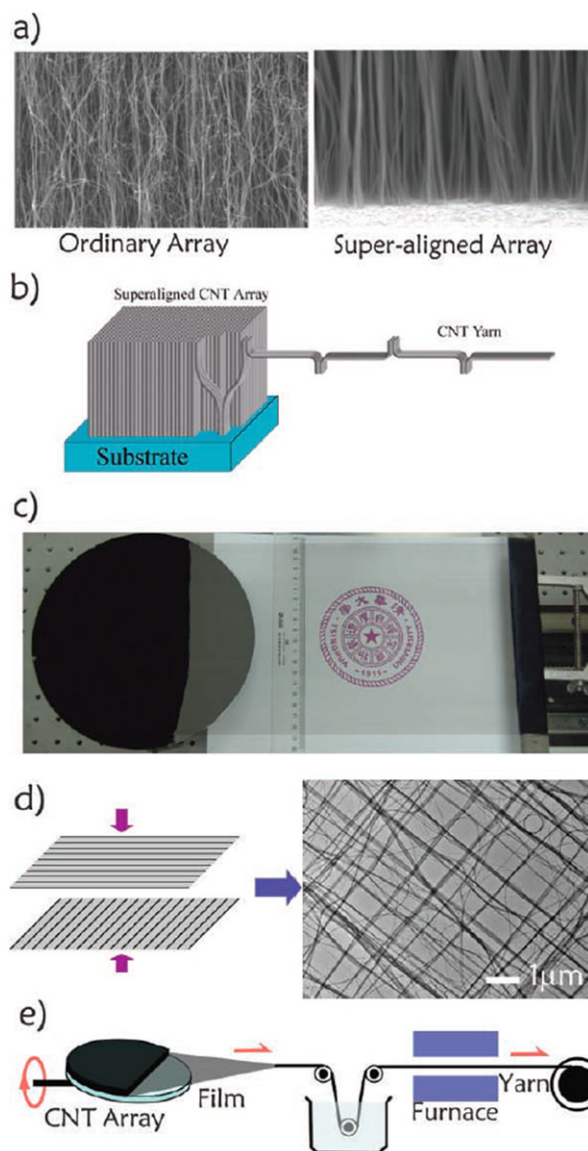


Figure 4. Processing method and films produced by the super-aligned CNTs. a–e) Reproduced with permission.^[116] Copyright 2011, Wiley-VCH.

mechanical strength, and good chemical stability. The combination of these unique properties makes graphene and GO good candidates for electrochemical energy-storage, including supercapacitors, batteries, fuel cells, and solar cells.^[41,46,57,138–141]

Chemically derived graphene obtained by the reduction of GO demonstrates various properties when reducing GO with different reduction agents and surfactants.^[142] Block copolymers poly(ethylene oxide)-poly(phenylene)-poly(ethylene oxide) PEO₁₀₆-PPO₇₀-PEO₁₀₆ (F127), as one of many investigated surfactants, self-assemble through hydrogen bonding to form mesoporous carbon structures.^[143] With thermal annealing, block copolymer modified GO with a specific surface area of $696 \text{ m}^2 \text{ g}^{-1}$ is fabricated, as shown in **Figure 6a**. The constructed supercapacitor, using the as-fabricated modified GO, shows a specific capacitance of 210 F g^{-1} .^[144] Graphene-based electrodes are reported

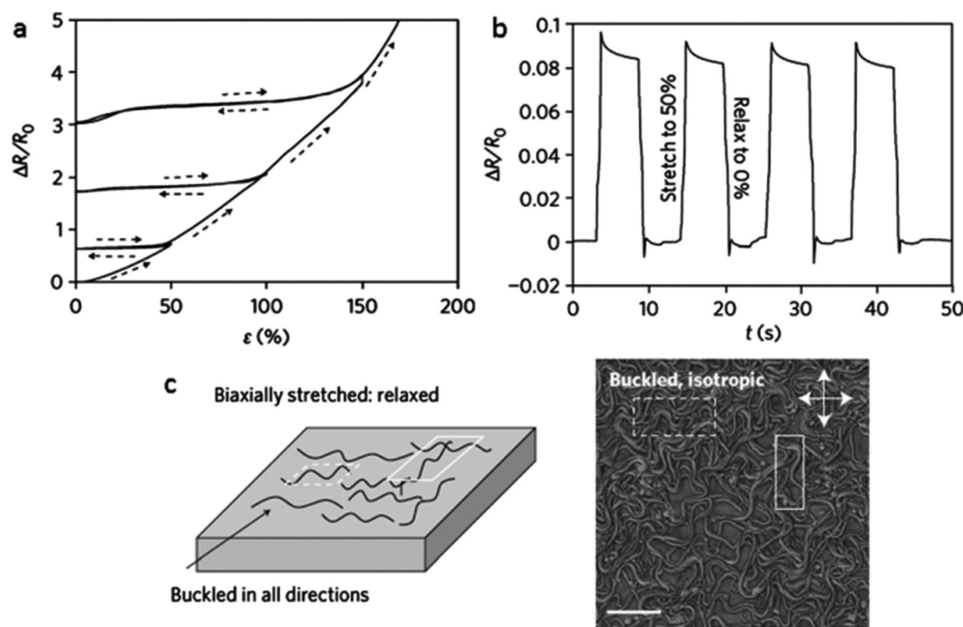


Figure 5. a) Change in resistance versus strain for CNT film on PDMS substrate. b) Cycling test for films stretched to 50%. c) Schematic and AFM image of buckled CNT film on PDMS. a–c) Reproduced with permission.^[126] Copyright 2011, Springer Nature.

utilizing both pristine graphene synthesized via CVD and multilayer rGO sheets prepared via chemical reduction of GO and layer-by-layer assembly, as shown in Figure 6b. All-solid-state 2D in-plane supercapacitors using a polymer-gel (PVA- H_3PO_4) electrolyte over the graphene electrodes show specific capacitance of $394 \mu\text{F cm}^{-2}$, higher than those obtained from stacked devices.^[145] Direct laser reduction of GO films to graphene is a much simpler method to produce mechanically robust, high electrical conductivity (1738 S m^{-1}), and specific surface area ($1520 \text{ m}^2 \text{ g}^{-1}$) films, as shown in Figure 6c. The produced films are directly used as supercapacitor electrodes without the need for binders or current collectors.^[146] The supercapacitors made by chemically derived graphene, GO and other carbon nanomaterials, or laser reduced GO not only show impressive electrochemical properties, but also provide a promising route to develop flexible all-solid-state supercapacitors due to the strong mechanical strengths and flexibilities of graphene/GO-based materials.

The development of graphene/GO-based materials for flexible supercapacitors focuses on the preparation methods of electrodes, electrochemical properties, and the flexibility of supercapacitors. As mentioned previously, freestanding graphene/GO-based electrodes exhibit a large surface area and high flexibility.^[46,145–147] In theory, the 2D sheets could provide surfaces for ionic exchange with the surrounding electrolyte with a low diffusion resistance. The high electrical conductivity of graphene sheets enables high energy density without the addition of conductive additives. The high aspect ratio of 2D materials, as in the freestanding graphene/GO-based electrodes, provides excellent mechanical flexibility.

The freestanding graphene/GO-based electrodes become relatively fragile when the thickness is less than $50 \mu\text{m}$. The surface of such freestanding electrodes is often not scratch resistant, limiting supercapacitors from practical usage. The me-

chanical properties are important for flexible supercapacitors used in stretching and folding applications. To solve this problem, the graphene/GO-based materials are coated onto a flexible substrate with excellent mechanical strength and flexibility.

Poly(ethylene terephthalate) (PET) is used as a substrate for flexible supercapacitors, due to its mechanical flexibility, lightweight, and thin thickness. An all-solid-state graphene-based in-plane interdigital micro-supercapacitor on PET substrate with a nanoscale thickness of 6–100 nm is reported (Figure 7). The resulting micro-supercapacitor delivers an areal capacitance of $80.7 \mu\text{F cm}^{-2}$ and a volumetric capacitance of 17.9 F cm^{-3} .^[148] Hybrid inks with 2D transition metal carbides, also known as MXene, nanosheets and electrochemically exfoliated graphene are demonstrated for the fabrication of flexible energy devices on flexible PET substrates (Figure 8). The achieved flexible micro-supercapacitor delivers a volumetric capacitance of up to 33 F cm^{-3} .^[149] In the MXene and graphene hybrid electrodes, the MXene flakes between graphene layers act as the active material for enhanced electrolyte shuttling and prevents π - π stacking between the graphene sheets.^[149,150]

In order to increase the specific surface area for supercapacitors, efforts are made to introduce porous flexible substrates for pore size control and 3D construction of graphene/GO-based supercapacitors. The presence of macropores, mesopores, and micropores is important for supercapacitors to deliver both high energy-storage capacity and high power delivery rate. Sponges, textiles, cellulose paper, etc. are used as flexible substrates for graphene/GO-based supercapacitors to enhance their electrochemical performances.^[151–153] Porous substrates are great material candidates for flexible substrates due to their excellent mechanical properties including high flexibility, lightweight, and high mechanical strength.

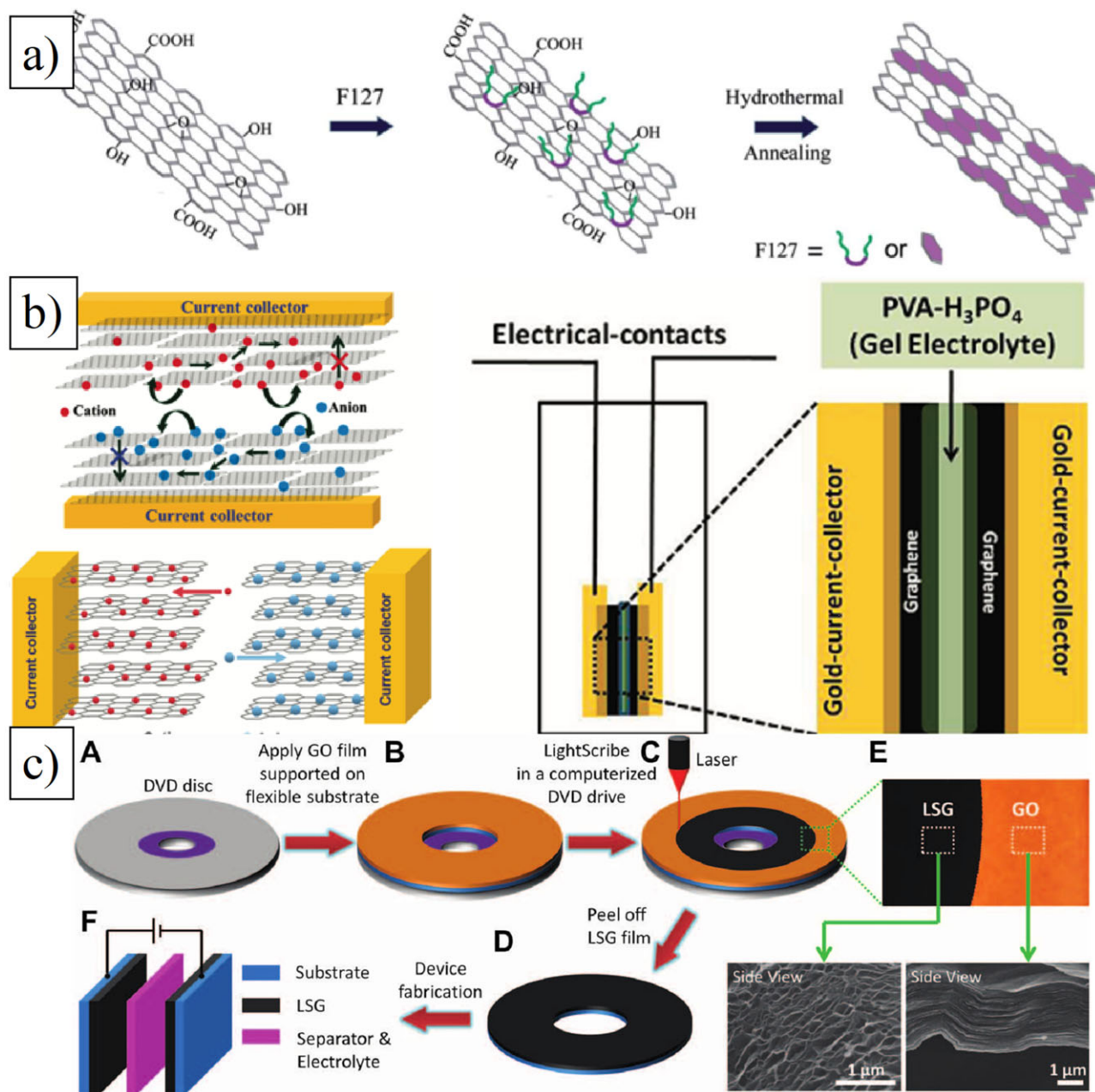


Figure 6. a) Illustration of the synthesis of rGO-F127 composites via hydrothermal and thermal annealing routes. b) Schematic of the stacked and in plane geometry of graphene-based electrode and all-solid-state supercapacitor devices with gel electrolyte. c) Schematic illustration of the fabrication of laser-scribed graphene-based electrochemical capacitors. a) Reproduced with permission.^[144] Copyright 2014, The Royal Society of Chemistry. b) Reproduced with permission.^[145] Copyright 2011, American Chemical Society. c) Reproduced with permission.^[146] Copyright 2012, American Association for the Advancement of Science.

Flexible supercapacitors are receiving tremendous research interest due to the ongoing revolution of electronic devices, especially toward flexible and wearable energy-storage devices. Due to the excellent mechanical and electrical properties, in addition to chemical stability, graphene and GO are thoroughly investigated and widely used for developing supercapacitors as either freestanding electrodes or with a flexible substrate. The functional groups on GO provide anchor points to attach other atoms,

molecules, nanoparticles, etc., enabling numerous opportunities to develop novel fabrication routes for supercapacitors.

3.2. CNT-Based Flexible Supercapacitors

Supercapacitors are electrochemical capacitors with the advantages of rapid charge/discharge rates, that is, high power

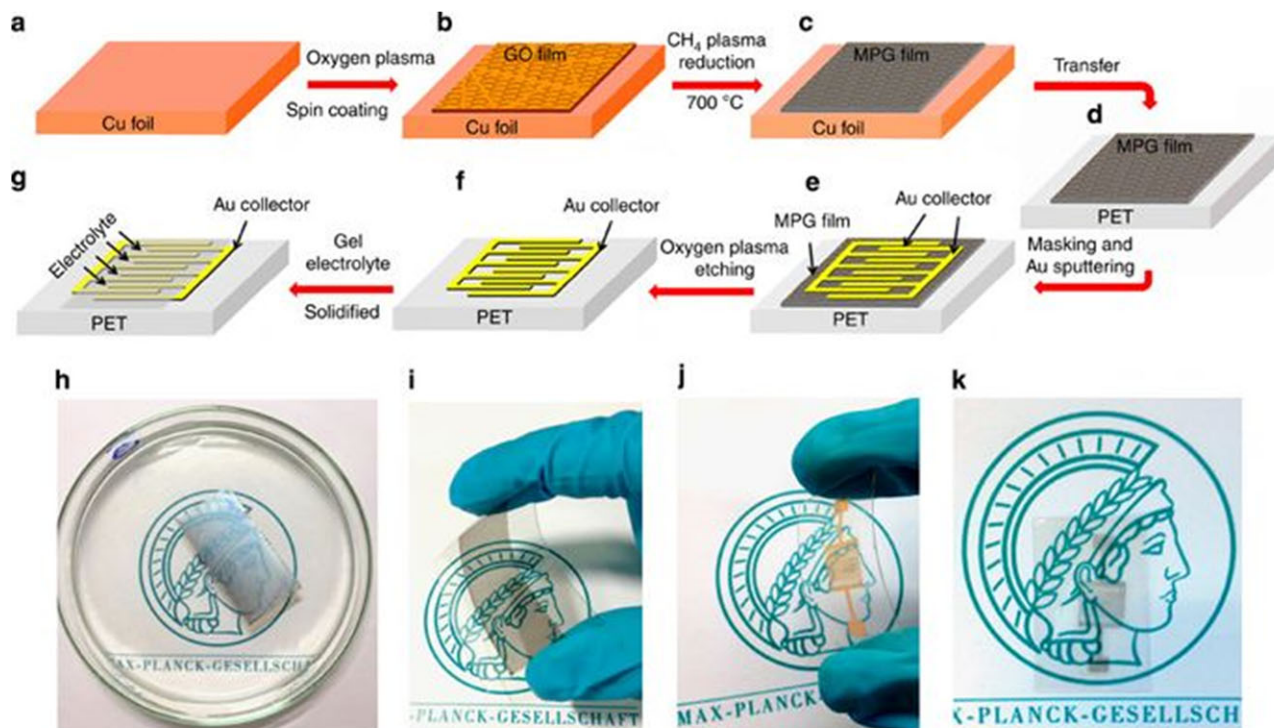


Figure 7. a–k) Schematic illustration of the fabrication of a flexible micro-supercapacitor using reduced graphene on PET substrates. a–k) Reproduced with permission.^[148] Copyright 2013, Springer Nature.

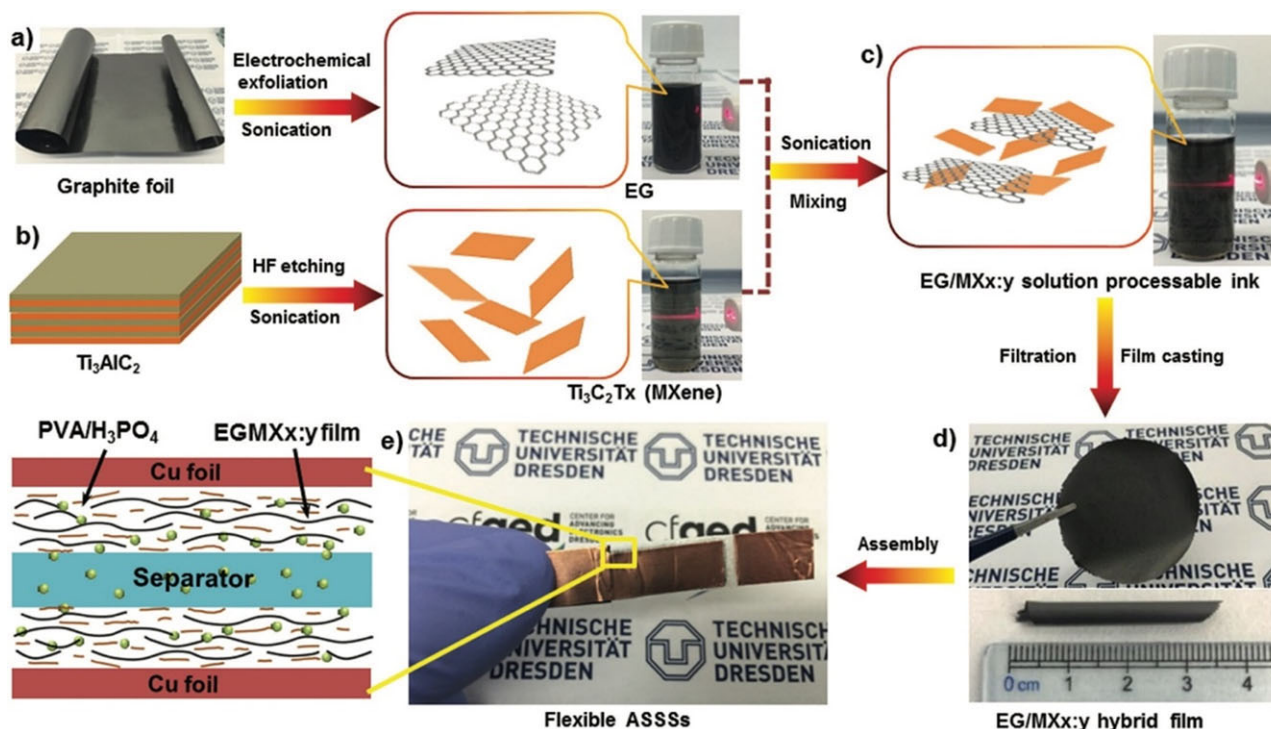


Figure 8. a–e) Schematic of the fabrication of flexible micro-supercapacitors using MXene and graphene hybrid material on a PET substrate. Reproduced with permission.^[149] Copyright 2016, Wiley-VCH.

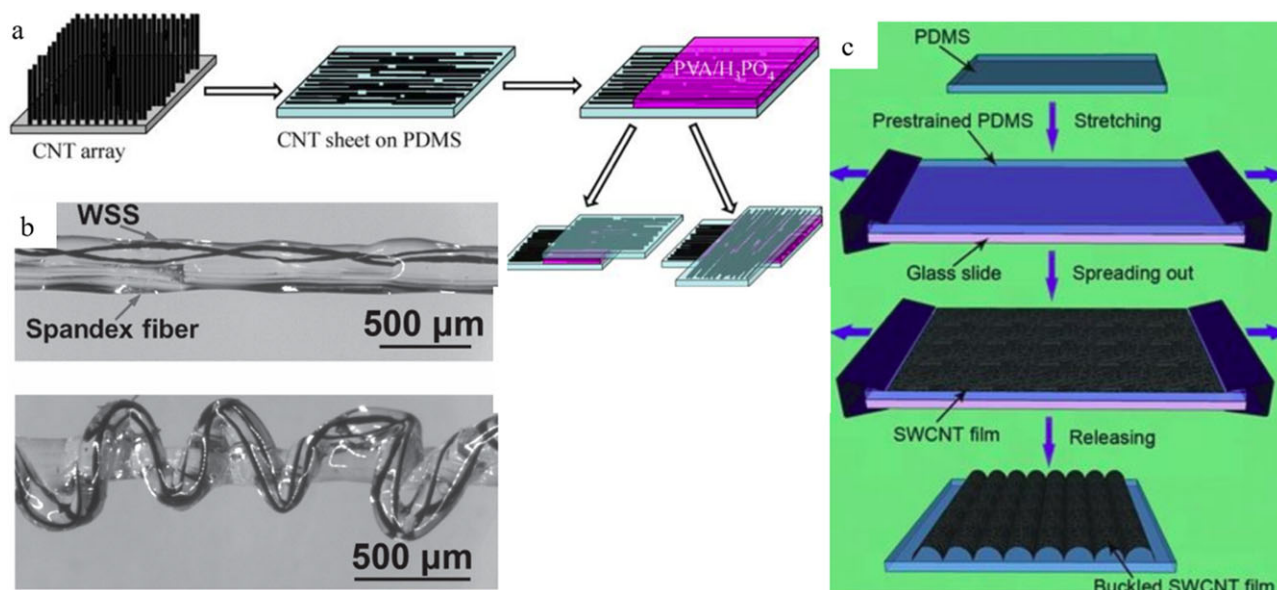


Figure 9. a–c) Typical examples of the flexible CNT-based EDLCs. a) Reproduced with permission.^[164] Copyright 2014, Springer Nature. b) Reproduced with permission.^[166] Copyright 2012, Wiley-VCH. (c) Reproduced with permission.^[184] Copyright 2013, Wiley-VCH.

densities and long cycle lifetimes.^[154–156] Supercapacitors have many possible applications, including portable devices, integrated energy sources, self-powered sensors, and wearable electronics.^[154,157,158] Supercapacitors are categorized as electric double layer capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors (i.e., combining both), based on the operation mechanisms. With the application of voltage, an EDLC forms an electric double layer at the interface between the electrode and the electrolyte. The distance between the electric double layers in the EDLCs is much smaller than that of conventional capacitors, which leads to typically several orders of magnitude higher capacitance.^[159] In comparison with EDLCs, pseudocapacitors usually involve electrochemical reactions; pseudocapacitance is accompanied by an electron charge-transfer between the electrolyte and the electrode, originating from a de-solvated and adsorbed ion. The bulk materials of the pseudocapacitor electrodes result in a higher capacitance, and therefore higher energy density, while the electron-transfer process leads to a slower charge/discharge rate than that of EDLCs.^[160,161]

CNTs are deposited on flexible substrates, such as papers,^[162] textiles,^[163] or polymer-based substrates,^[111] by directly stacking onto substrates,^[164–166] transfer,^[167] drop-dry,^[162] printing,^[168] out-of-plane growth,^[169] or spray coating.^[170] With a high specific surface area of $100 \text{ m}^2 \text{ g}^{-1}$, EDLCs using SWCNTs with a diameter $\approx 100 \text{ nm}$ show a volumetric capacitance of 16.6 F cm^{-3} and energy density up to 20 Wh kg^{-1} .^[171] The capacitance is enhanced by at least $\approx 100\%$ by methods of heating,^[172,173] chemical activation,^[174–176] functionalization,^[176–178] or shape engineering.^[179] Key factors determining the performance of supercapacitors constructed using SWCNT electrodes include composition of the binder, annealing temperature, types of current collector, charging time, and discharging current density.^[180] Pure CNT-based EDLCs show high rate capabilities, long cyclic lifetime, and rectangular cyclic voltammograms with symmetric triangular galvanostatic charge/discharge profiles, which indi-

cate high electrochemical performance.^[181,182] Examples of CNT-based flexible EDLCs are shown in **Figure 9**. Several fabrication strategies are developed to increase the flexibility of EDLCs. SWCNT films with continuous reticulate architecture are combined with PDMS for enhanced pre-strain, and achieves highly stretchable buckled SWCNT films, which operate under a strain of 140% without any significant change of the resistance.^[166] Vertically aligned CNTs embedded into PDMS as the flexible electrodes for EDLCs demonstrate a stretchability of 200%.^[111] Highly aligned CNTs are used to develop high-performance transparent and stretchable supercapacitors with a transparency up to 75% and a specific capacitance of 7.3 F g^{-1} .^[164] The aerosol synthesized and dry deposited SWCNT thin films used as electrodes for EDLCs exhibit extremely large specific capacitance of 178 F g^{-1} , areal capacitance of $552 \text{ } \mu\text{F cm}^{-2}$, high optical transparency (92%), and stability for 10 000 charge/discharge cycles.^[183] As demonstrated, CNTs are promising materials to construct high-performance flexible supercapacitors.

CNTs are also combined with other active components, such as conducting polymers (polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene)) or metal oxides (MnO_2 , TiO_2 , RuO_2), as the electrodes for flexible pseudocapacitors.^[107,120,163,188–193] These flexible pseudocapacitors show a high capacitance, such as CNT-PPy with a capacitance of 0.28 F cm^{-2} , which is much higher than EDLC.^[194] Several examples of CNT-based flexible pseudocapacitors are shown in **Figure 10**. Conducting polymers and CNT composites often possess both good electric conductivity, high capacitance, increased flexibility and long lifetime. A graphene/ MnO_2 /CNT nanocomposite shows outstanding mechanical properties (tensile strength of 48 MPa) and superior electrochemical activity that are not achieved by any of these components alone.^[120] Conducting polymer/ MnO_2 on CNT textile prevents delamination of MnO_2 nanoparticles, showing an increase of 38% in the electrochemical energy capacity with an improved cyclic reliability of 750 000 bending cycles.^[163] A

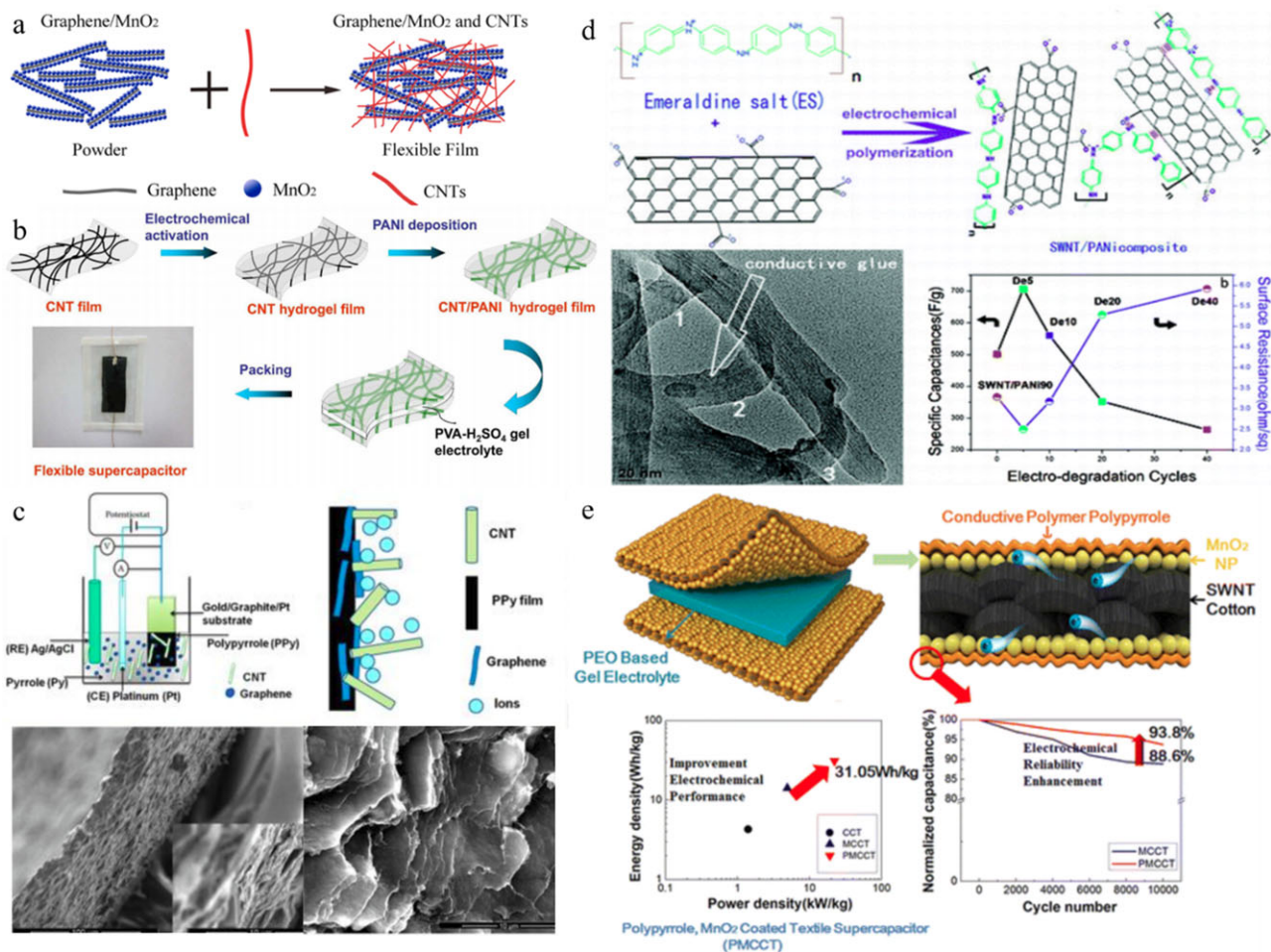


Figure 10. Typical examples of flexible CNT-based pseudocapacitors. a) Reproduced with permission.^[120] Copyright 2012, American Chemical Society. b) Reproduced with permission.^[185] Copyright 2015, The Royal Society of Chemistry. c) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>).^[186] Copyright 2015, Springer Nature. d) Reproduced with permission.^[187] Copyright 2010, American Chemical Society. e) Reproduced with permission.^[163] Copyright 2015, American Chemical Society.

fiber-shaped supercapacitor using two aligned CNT/polyaniline composite sheets as electrodes demonstrates stretching of over 400% with a high specific capacitance of approximately 79.4 F g^{-1} .^[195] The CNT carpet is used as the substrate to load active materials and/or current collector to ensure high capacitance and rapid charge transfer for high-performance pseudocapacitors.

4. Graphene- and CNT-Based Flexible Batteries

4.1. Flexible Battery Electrodes

Rechargeable batteries, especially modern Li-ion batteries that offer large energy densities with low failure rates and long operational times, are promising for energy-storage applications currently employed by high-tech portable electronics and long-range electric vehicles.^[196] Flexible (micro) devices, including wearable electronics, foldable displays, implantable biomedical devices, and micro-sensors, open a new horizon for the future of battery applications, thereby attracting huge re-

search attention.^[197] However, from the perspective of materials design, it is nontrivial to make flexible batteries due to the rare availability of electrochemical compounds that offer desirable mechanical properties.^[196] In addition, maintaining mechanical integrity between different battery components, such as electrodes, electrolytes, and current collectors, is a complicated problem.

Battery electrodes are in general thick films (from tens to hundreds of micrometers thick) made of composite materials, including: 1) an active material that stores charge carriers (alkali metal or multivalent ions) and electrons, 2) a conductive phase that serves as electronic pathways, and 3) a binder that stitches everything together. Many carbon allotropes, including graphite, hard carbon, graphene, rGO, and CNT, are used as active materials in the conventional battery electrodes due to their desirable electrical properties, good electrochemical activity, and chemical stability.^[198,199] Graphene and CNT-based materials may be best used for flexible anodes, replacing graphite that is currently used in Li-ion batteries. Since recent decades, optimized (electro)chemical and mechanical properties of these

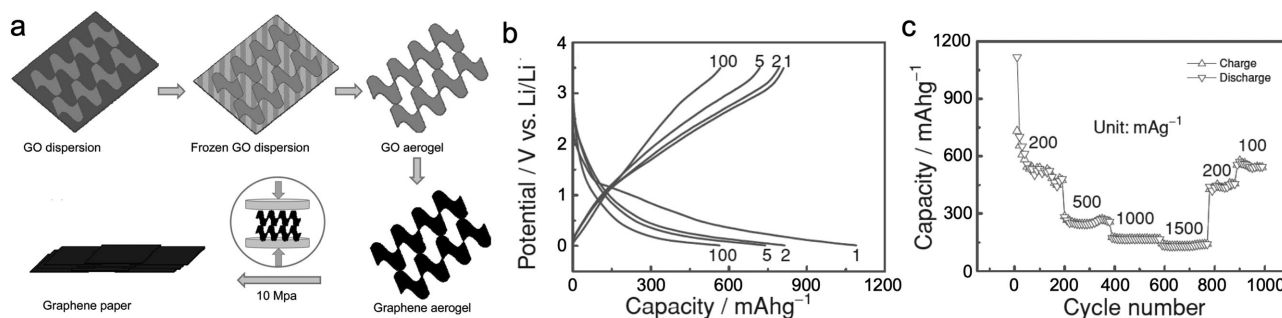


Figure 11. a) A scheme for fabrication of folded graphene, b) its charge and discharge profiles, and c) its rate capability over an extended number of cycles. a–c) Reproduced with permission.^[218] Copyright 2012, Wiley-VCH.

materials continue to be intensively investigated.^[200–205] An additional benefit of using these materials includes a simplistic electrode design; due to superb electrical conductivity and intrinsic flexibility, anodes composed of graphene and CNT-based materials often do not require a Cu current collector or a polymer binder during electrode fabrication.^[206] For cathodes, they are used as conductive phases, rather than the active component due to low-charge storing potential (i.e., voltage), though some exceptions exist.^[207,208] Although graphene and CNT-based materials are also combined with non-flexible materials to provide supplemental flexibility at the device level, we will not cover them here unless they are directly related to charge storage activity. Also, how to engineer battery packaging for flexible device applications is found elsewhere.

4.2. Charge-Storage Mechanism in Graphene and CNTs

Graphene and CNT-based materials store more lithium ions per unit mass than graphite.^[209,210] In graphite, six carbon atoms typically host one Li, forming a nominal composition of LiC_6 upon full charging. Therefore, the theoretical amount of Li that is reversibly intercalated per unit mass of graphite (i.e., specific capacity) is 372 mAh g^{-1} .^[211] The predicted capacities of graphene and CNT-based anodes, $\approx 1110 \text{ mAh g}^{-1}$, are much larger than that of graphite as two carbon atoms are enough to host one Li leading to nominal LiC_2 stoichiometry at a fully charged state theoretically.^[209,210] According to recent reports,^[212,213] however, further investigation on the charge storing mechanisms and Li hosting chemistries for these materials is necessary, which will be discussed in the next subsection.

4.3. Graphene as a Main Active Material

Owing to excellent mechanical properties^[23,214] and high electron conductivity, graphene and CNT-based materials are used as flexible anodes.^[203,215–217] One of the industrially applicable forms of anodes is graphene paper as shown in **Figure 11**, which achieves high capacity ($>500 \text{ mAh g}^{-1}$).^[218] Graphene papers are prepared by vacuum filtration of an aqueous dispersion of rGO.^[32] However, capacities reported in early studies are around 250 mAh g^{-1} .^[212] In addition, these graphene papers suffer from

poor capacity retention over an extended number of cycles. Cyclic voltammetry shows an irreversible reduction at around 1.5 V, likely originating from residual functional groups of rGO and/or reaction byproducts upon synthesis.^[212,213] This also explains large variations in the electrochemical performance of graphene paper anodes produced by different methods and functionalized by different additives.^[219,220] The reduction process of rGO results in highly aligned morphology that enables a high Young's modulus and high electrical conductivity.^[221] Also, strategically selecting proper spacer materials including polymer chains and metal oxide nanoparticles to adjust the arrangement between the graphene sheets improves the Li intercalation kinetics for graphene paper anodes.^[222,223] Direct modification of graphene often improves its electrochemical properties as an electrode material. Holey graphene with in-plane pores produced via ultrasonication and acidic treatment can be used as an electrode.^[204] Li diffusion through the pores improves the apparent transport of the cell, allowing high-rate cycling. Similarly, cracks and voids that exist on the graphene layer may enhance Li kinetics. It is also reported that the formation of porous graphene sheets from mechanically pressed graphene aerogels enhances the electrochemical properties of graphene-based materials. In **Figure 11**, the anode shows large capacities of 557, 268, and 141 mAh g^{-1} at current densities of 200, 500, and 1500 mA g^{-1} , respectively, which is explained by the effect of graphene folding that proliferates the number of activated sites for Li storage.^[218] Doping can generate atomic defects that boost the electrochemical activity of graphene electrodes.^[224] As shown in **Figure 12**, a nitrogen-doped graphene anode shows a remarkably high capacity of 1043 mAh g^{-1} in the first cycle and 872 mAh g^{-1} in the 30th cycle at a current density of 50 mA g^{-1} .^[225]

4.4. CNTs as a Main Active Material

For battery applications, CNTs are also fabricated into a thin paper form. Similar to the graphene paper anodes, it requires substantial optimization efforts to achieve desirable electrochemical performance. Among a wide variety of preparation methods for CNT papers such as drop-casting, spray-coating, and spin-coating,^[226–229] vacuum filtration of CNT dispersions supplemented by surfactant treatment offers the most promising electrochemical properties.^[62] CNT papers prepared by mechanical pressing lead to controlled morphologies with a preferred

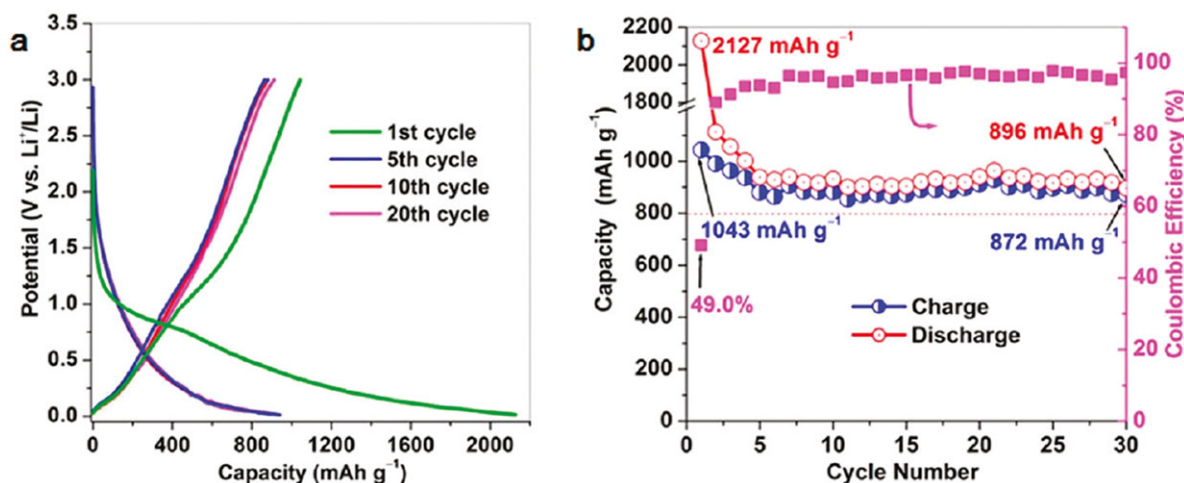


Figure 12. a) Galvanostatic charge and discharge profiles, and b) cycle performance and Coulombic efficiency of a N-doped graphene electrode at a low current rate of 50 mA g^{-1} between 3.0 and 0.01 V versus Li metal. a,b) Reproduced with permission.^[225] Copyright 2011, American Chemical Society.

orientation.^[230] The electrochemical performance of CNT papers depends on their kinds and/or synthesis methods. For instance, anodes made of single-wall carbon nanotubes (SWCNTs) result in 200 mAh g^{-1} , at most, over an extended number of cycles.^[231,232] In addition, a substantial amount of parasitic reactions are found in the first cycle, likely due to numerous defects in the SWCNT films, as well as a high surface area ($435 \text{ m}^2 \text{ g}^{-1}$) and high mesopore volume ($0.75 \text{ cm}^3 \text{ g}^{-1}$), which may lead to excessive electrolyte decomposition and solid–electrolyte interphase (SEI) formation.^[231] Improved Li intercalation behaviors for CNT paper anodes can be achieved by controlling the morphology of CNT walls.^[231] Compared with anodes made of SWCNTs and double-wall carbon nanotubes (DWCNTs), multi-wall carbon nanotubes (MWCNTs) paper anodes exhibit better performance, rivaling disordered carbon, due to their reduced specific area ($50 \text{ m}^2 \text{ g}^{-1}$) and mesoporosity ($0.13 \text{ cm}^3 \text{ g}^{-1}$).^[231] Improved capacity is achieved with CNTs integrated with carbon layers produced by chemical vapor deposition (CVD)^[203] due to high in-plane conductivity of the carbon layers in direct contact with the CNT layers. Electrodes consisting of CNTs on the carbon layers show large and reversible capacities (572 mAh g^{-1} after the 100th cycle) attributed to the superior physical integrity between the two components providing superior conductivity.^[203] The capacity retention of CNT paper anodes tends to vary with the composition of electrolytes used as a result of its direct impact on the SEI formation. A ternary mixture of ethylene carbonate, propylene carbonate, and diethyl carbonate promotes reversibility of CNT anodes compared with a binary mixture of ethylene carbonate and dimethyl carbonate, implying that the opportunities to fully employ CNT-based electrodes for flexible batteries may also lie in the development of appropriate electrolytes.^[198] It should be noted that the chemical and physical properties of CNTs are highly dependent on the surface characteristics.^[233] Therefore, there is room even to modify the redox reaction of CNTs by controlling their surface functional groups. The electrochemical performance of the functionalized CNT paper varies with surface oxidation,^[207,208] and oxygen functional groups in CNTs result in high redox potential, as shown in **Figure 13**. Lee et al. claimed

that electrons are donated from and accepted by the double bonds at carbonyl groups, as similarly observed with organic Li cathode materials consisting of aromatic rings.^[234,235] As a cathode, these electrodes show reasonable specific capacity of $\approx 200 \text{ mAh g}^{-1}$ at 0.4 A g^{-1} with an average voltage of $\approx 3 \text{ V}$ versus Li metal.

Recent results highlighting improved electrochemical performances such as high power and long-term cycle life of graphene and CNT-based battery electrodes show a great prospect toward the development of flexible systems. Their electrochemical and mechanical properties depend on synthesis methods and surface functionalization, offering substantial affordability in materials design to improve energy-storage performance as self-standing electrodes. More importantly, graphene and CNT-based electrodes may be combined with state-of-the-art solid electrolytes, enabling all-solid-state flexible batteries that eliminate the packaging issues of flowing carbonate-based liquid electrolytes and the safety concern of flammability of the carbonate liquids.

5. Summary and Perspectives

Flexible and stretchable energy-storage devices are critical for the next generation of wearable and portable electronic devices, flexible displays, and monitoring systems. Micro/nanostructures and composites of carbon nanomaterials with other active materials are used to develop flexible supercapacitors and batteries. Here, the recent development and progress of flexible supercapacitors and batteries based on graphene/GO and CNTs are discussed.

In the materials perspective, graphene, GO, and CNT-based electrodes have a great opportunity for flexible energy-storage applications due to their inherent mechanical flexibility, excellent electrochemical properties, and chemical stability. Although promising, there are obstacles to overcome, such as high materials costs, non-scalable processes, and size-dependent properties, which may limit their employment across various applications. First, pure carbon materials such as graphene, GO, and CNTs

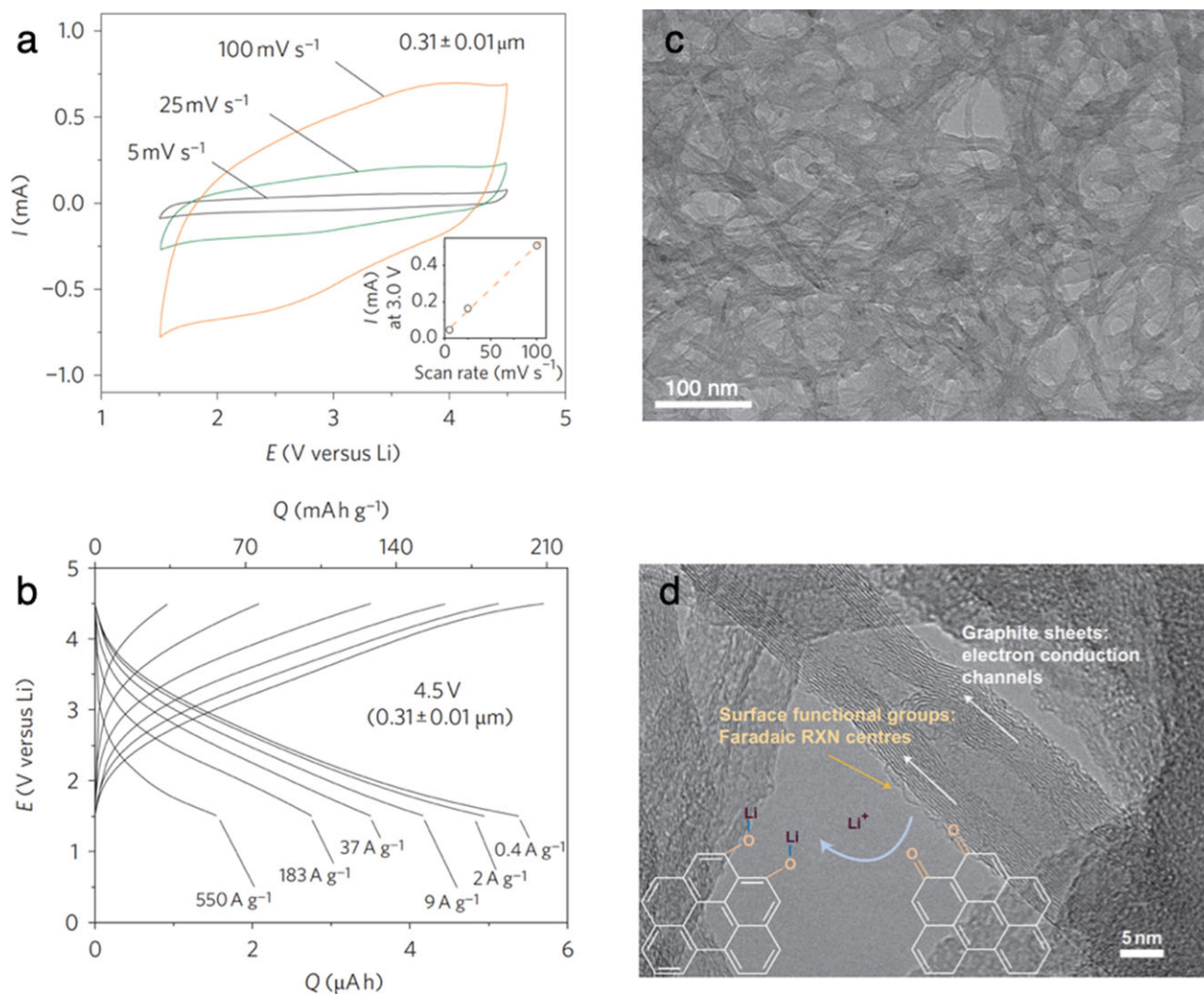


Figure 13. a) Cyclic voltammogram and b) galvanostatic charge and discharge profiles as a function of charge with respect to current density for layer-by-layer MWCNT electrodes against Li metal with 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (3:7 by volume). TEM images of a layer-by-layer MWCNT electrode slice with c) low magnification and d) high magnification overlaid by a schematic describing the proposed energy-storage mechanism. a–d) Reproduced with permission.^[207] Copyright 2010, Springer Nature.

are known to have a lower capacitance compared to conducting polymer materials or metal oxides. Therefore, there is a need to combine those carbon materials with other active materials as composite electrode materials for developing high-performance batteries and supercapacitors. Second, several problems involving the fabrication process of flexible electronic devices need to be addressed, including the delamination, leakage of the liquid electrolyte, a separator to avoid internal short circuiting, and encapsulation. Third, the properties of these flexible energy-storage devices will be changed by the mechanical deformation, and the structural design of flexible energy-storage devices will influence the mechanical properties and therefore overall performance. Finally, industrial considerations of these flexible batteries and supercapacitors, such as the weight, volume, and cost, need to be further improved for commercial applications. When designing flexible power sources, the size should be sufficiently small, and carbon-based materials, which are utilized as current collectors,

have a relatively low conductivity compared to metal current collectors, which are widely used in traditional electrodes.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

batteries, carbon nanotubes, flexible devices, graphene, graphene oxide, supercapacitors

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