Facile Fabrication of Flexible Supercapacitors for Wearable Applications

Yuqing Liu

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Facile Fabrication of Flexible Supercapacitors for Wearable Applications

Yuqing Liu

This thesis is presented as part of the requirements for the Award of the Degree of Doctor of Philosophy of The University of Wollongong

June 2018
Certification

I, Yuqing Liu, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, at the Australian Institute for Innovative Materials, University of Wollongong, is wholly my own work except where specific references or acknowledgements are made. The thesis has not been submitted for a degree to any other university or institution.

Yuqing Liu

June 2018
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Finally, I owe my achievements to my beloved parents. I thank them for giving me life, raising me up and teaching me about life. Also thanks for their endless love and support.
PUBLICATIONS


ABSTRACT

The need to develop next-generation wearable electronics in various fields has promoted the development of flexible and lightweight supercapacitors with high performance. Great progress has been made in developing flexible electrode materials, seeking stable and efficient gel polymer electrolytes and investigating different device architectures. However, it is still a main challenge to develop flexible electrodes on a large-scale and in a cost-effective manner. In addition, supercapacitors with interdigitated electrodes exhibit superior performance (i.e. higher energy and power density) in a limited space than the traditional sandwiched design with film electrodes and are more suitable to be integrated to the increasingly miniaturized wearable electronics. Nevertheless, the additional electrode patterning step exerts pressure on developing simple and scalable patterning techniques and selecting technically compatible electrode materials.

The main goal for this study is to develop high performance electrodes (in the form of both film and interdigitated patterns) for flexible supercapacitors in simple and scalable ways. A flexible, large-size and free-standing reduced graphene oxide (rGO)-poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) film was firstly prepared via a simple bar-coating method and assembled to be flexible all-solid-state supercapacitors. A high areal capacitance of 448 mF cm$^{-2}$ can be achieved at a scan rate of 10 mV s$^{-1}$ using the composite electrode with a commercial level mass loading of 8.49 mg cm$^{-2}$, indicating the potential to be used in practical applications. To demonstrate the applicability, a roll-up supercapacitor device was constructed, which illustrated the operation of a green LED light for 20 seconds when fully charged.
In the following work, a simple laser-etching process was applied on the large-size rGO-PEDOT/PSS film to generate interdigitated micro-electrodes. The fabricated flexible microsupercapacitors (fMSCs) from the interdigitated micro-electrodes shows superior capacitance to the fMSCs from the traditional sandwiched design when normalized to the volume of the whole device, indicating the significance of the additional laser-etching process. The performance of the fMSC was further optimized after tuning the micro-electrode design (i.e. width and thickness of electrode), which can display a high areal capacitance (84.7 mF cm\(^{-2}\) at 5 mV s\(^{-1}\) and 45.5 mF cm\(^{-2}\) at 200 mV s\(^{-1}\)), volumetric capacitance (14.5 F cm\(^{-3}\) at 5 mV s\(^{-1}\) and 7.83 F cm\(^{-3}\) at 200 mV s\(^{-1}\)), and excellent cycling stability (>10 000 cycles). These values are comparable with literature reported carbon-based fMSCs with high performance. We also demonstrate the simplicity and speediness of the fabrication process via etching 10 fMSC patterns in just 100 seconds. The demonstration of powered LED lights using the single and tandem fMSCs highlights the great potential of the scalable fMSCs in real application.

The performance of fMSCs was further improved via incorporating pseudo-capacitive materials of polyaniline (PANi) and employing an asymmetric design. To achieve this aim, another simple and scalable patterning technique of extrusion printing was used, and highly concentrated, viscous, and water-dispersible inks containing active materials were developed for this reason. Inks comprising hierarchical structured graphene oxide (GO)/polyaniline composite were developed via using the PEDOT/PSS as dispersing agent. The rGO-PEDOT/PSS dispersion used in the previous work was also modified to be printable. We found that the extrusion printed GO/PANi-PEDOT/PSS fMSCs deliver much higher capacitance than the rGO-
PEDOT/PSS fMSCs, and can deliver outstanding an improved areal capacitance of 153.6 mF cm$^{-2}$ and volumetric capacitance of 19.2 F cm$^{-3}$ at 5 mV s$^{-1}$. Moreover, by fabricating asymmetric fMSCs using the GO/PANi-PEDOT/PSS as positive electrode and rGO-PEDOT/PSS as negative electrode, we can widen the voltage window from 0.8 to 1.2 V and achieve improvements in energy density (from 3.36 to 4.83 mWh cm$^{-3}$), power density (from 9.82 to 25.3 W cm$^{-3}$) and cycling stability (from 75 % to 100 % capacitance retention over 5000 cycles) compared with the symmetric counterpart. The simple ink preparation and facile device fabrication protocols reported here make the scalable fabrication of extrusion printed fMSCs a promising technology.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>APS</td>
<td>Ammonium persulfate</td>
</tr>
<tr>
<td>C</td>
<td>Coulomb</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CPs</td>
<td>Conducting polymers</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>DEG</td>
<td>Diethylene glycol</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electrochemical double-layer capacitor</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>GCD</td>
<td>Galvanostatic charge/discharge</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>F</td>
<td>Farad</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>iR</td>
<td>Resistance drop (V)</td>
</tr>
<tr>
<td>M</td>
<td>Mole per litre</td>
</tr>
<tr>
<td>m</td>
<td>Metre</td>
</tr>
<tr>
<td>mA</td>
<td>Milliampere</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>MSCs</td>
<td>Micro-supercapacitors</td>
</tr>
<tr>
<td>mV</td>
<td>Millivolt</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre</td>
</tr>
<tr>
<td>Pa</td>
<td>Pascal</td>
</tr>
<tr>
<td>PANi</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly (dimethylsiloxane)</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>Poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Terephthalate</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly (vinyl alcohol)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>S</td>
<td>Siemens</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SCs</td>
<td>Supercapacitors</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SSCs</td>
<td>Sandwiched structured supercapacitors</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotube</td>
</tr>
<tr>
<td>R&lt;sub&gt;ct&lt;/sub&gt;</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>t</td>
<td>Time (usually in seconds unless otherwise stated)</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>V</td>
<td>Volt</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Ω</td>
<td>Ohm</td>
</tr>
<tr>
<td>µ</td>
<td>Micro</td>
</tr>
</tbody>
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Chapter 1  Introduction
1.1 Principle of supercapacitor

Supercapacitors (SCs), also called electrochemical capacitors or ultracapacitors, are an important sector in energy storage systems. The family of capacitors are based on charging and discharging at electrode-electrolyte interface of high surface area materials, such as porous carbons or metal oxides. To date, progress has been made in developing energy storage systems such as lithium-ion batteries and SCs for diverse applications in personal consumer electronics, electric vehicles, and uninterruptable power supplies. Lithium-ion batteries were commercialized by SONY in 1990. As illustrated in Figure 1.1, they can achieve an energy density as high as 180 Wh kg⁻¹. However, Lithium-ion batteries suffer from slow power delivery or uptake, which inhibits their applications in energy storage systems where fast and high power is needed. Conversely, conventional capacitors have a much higher power density than batteries, but their energy density lower. SCs have the potential to bridge the gap between batteries and conventional capacitors. A typical supercapacitor shows an energy density of ~5 Wh kg⁻¹, which is lower than that of batteries, but a much higher power density of ~10 kW kg⁻¹ can be achieved in a few seconds. Significant efforts have been made recently to increase the energy density of the SCs to be close to or beyond that of the batteries without sacrificing their high power density.

SCs are generally classified into two types based on their energy storage mechanisms: (1) electrochemical double-layer capacitor (EDLC), which stores energy by the adsorption of anions and cations on the surface of electrodes; (2) pseudo-capacitor which derive the capacitance from the storage of charge in redox materials in response to a redox reaction.
Figure 1.1 Ragone plot for various types of energy storage devices. Reproduced with permission[1]. Copyright 2008, Rights Managed by Nature Publishing Group.

1.1.1 Electric double layer capacitors (EDLC)

The first EDLC was demonstrated and patented by General Electric in 1957.[3] Generally, EDLC is composed of two carbon based electrodes with high surface area, an electrolyte and a separator (Figure 1.2a). When the supercapacitor is charged, cations in the electrolyte move to the negatively polarized electrode, and anions migrate to the positively polarized electrode. The concept of a double layer was first described by Helmholtz in 1853, who stated that two layers of opposite charge form at the electrode-electrolyte interface. This simple model was then refined by Gouy and Chapman; they introduced a diffuse layer, which arose from the accumulation of ions close to the
electrode surface. However, the Gouy-Chapman model overestimated the EDLC capacitance since the capacitance increases inversely with the separation distance. Later, Stern combined these two models to define the two parts of ion distribution; the compact layer and the diffuse layer. In the compact layer, the hydrated ions are adsorbed strongly by the electrode, and the compact layer is composed of specifically adsorbed ions and non-specifically adsorbed counter ions. The diffuse layer is what the Gouy-Chapman model has defined. The capacitance in the EDL can be considered as a combination of the capacitances from the compact and diffuse layers (Figure 1.2b).\[^4\] The capacitance of an EDLC is generally given by the following equation (Equation 1.1) for a plate capacitor:

\[
C = \frac{\varepsilon_r \varepsilon_0 A}{d}
\]

\textbf{Equation 1.1}

where \(\varepsilon_r\) is the dielectric constant of the electrolyte, \(\varepsilon_0\) is the dielectric constant of vacuum, \(A\) is the surface area of the electrode which is accessible to the electrolyte ions, and \(d\) is the effective thickness of the double layer. However, some work revealed that the specific capacitance and the surface area do not show a linear relationship.\[^5,6\] This nonlinearity is ascribed to the presence of some micropores that are inaccessible to large solvated ions. Huang and co-workers accounted for this pore distribution and separated the capacitance according to pore size.\[^7\] Their models fit well with the experimental results, no matter what type of carbon materials and electrolytes are employed. To date, various carbon materials such as activated carbon, carbon nanotubes and graphene are the most widely used active electrode materials due to their high specific surface area, high conductivity, easy processing and high chemical stability.
In contrast to EDLCs, a pseudo-capacitor stores energy through fast and reversible redox reactions between the electrolyte and the electrode materials. When a potential is applied to a pseudo-capacitor, redox reactions occur on the electrode materials and the charge passes across the double layer, resulting in a current passing through the supercapacitor.\textsuperscript{[8]} The typical electrode materials for this kind of supercapacitor include conducting
polymers\textsuperscript{[8]}, and metal oxides or hydroxides\textsuperscript{[9]}. The charging process of conducting polymers can be expressed as follow:

\[
CP \rightarrow CP^n^+(A^-)_n + ne^-
\]

The anions in the electrolytes transfer into the backbone of polymer chains. During discharging, the anions are ejected from the backbone and migrate into the electrolyte.

Among metal oxides with pseudo-capacitance, Ruthenium oxide (RuO\textsubscript{2}) is the most promising material. This is due to its conductive and very high theoretical specific capacitance of \(\sim 2000\) F g\textsuperscript{−1}.\textsuperscript{[2]} In acidic electrolytes, the oxidation states of Ru can change from Ru (II) to Ru (IV), which involves rapid reversible electron transfer together with the electron-adsorption of protons on the surface of RuO\textsubscript{2}. This process can be described by the reaction below\textsuperscript{[10]}.

\[
RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x , \text{ where } 0 \leq x \leq 2.
\]

### 1.1.3 Hybrid system

Pseudo-capacitive materials exhibit much higher capacitance than EDLC-type carbon materials, while suffering poor electrochemical stability. To overcome this problem, composites comprised of both type of materials are prepared, which utilize the above two mechanisms and exhibit excellent performance (\textit{i.e.}, in both capacitance and cycling stability) from the synergistic effect of the two components.\textsuperscript{[11,12]}

Another approach to solve this problem is the use of an asymmetric configuration, which uses electrodes with different nature for positive and negative polarization.\textsuperscript{[11,13]}
asymmetric SCs, carbon-based materials are usually used as negative electrodes, while pseudo-capacitive materials (i.e., conducting polymers or metal oxides) are selected as positive electrodes. It is generally believed that the operating window of symmetric SCs (i.e., using the same material in both electrodes) hardly exceeds 1 V in aqueous electrolyte.\cite{14} However, combining the operating potential range of the two kinds of materials, asymmetric SCs can extend the voltage range up to 2.2 V without the decomposition of aqueous electrolyte, which can greatly enhance the energy and power density of a supercapacitor device.\cite{14} Meanwhile, with each electrode operating in its optimal potential range, the cycling stability can also be enhanced.

1.2 Flexible SCs

In order to meet the functional demands for next-generation digital roll-up displays, flexible photovoltaic cells, and wearable devices, the development of high-performance SCs that have excellent flexibility and stable performance is essential. Most studies on SCs have primarily focused on using liquid electrolytes, such as aqueous solutions, organic solutions and ionic liquids.\cite{14} Since most of these liquid electrolytes are toxic and corrosive, precise packaging is required to avoid any possible leakage of these electrolytes. An alternative solution to leakage challenge is the use of solid-state electrolyte. This configuration can also lead to reduced packaging costs. Flexible solid-state SCs present important advantages over traditional ones, which include miniaturization and flexibility, decreased weight, improved energy and power density, and ease of handling. These advantages make them a promising new class of energy storage devices for flexible and wearable electronics.
A flexible solid-state supercapacitor is generally composed of flexible electrodes, a solid-state electrolyte and a flexible packaging material. The flexible electrode should have high capacitance, low self-discharge, long cycling stability and high mechanical stability. The solid-state electrolyte needs to possess a high ionic conductivity, thermal and mechanical stability. The solid-state electrolyte can also serve as the separator eliminating the need for an additional separator.\textsuperscript{15}

\textbf{1.2.1 Potential electrode materials}

\textit{1.2.1.1 Carbon materials}

Carbon nanomaterials such as 1D carbon nanotubes (CNTs) and 2D graphene, with structures composed of conjugated sp\textsuperscript{2} carbons, have been widely studied for flexible energy storage applications.\textsuperscript{16}

CNTs are a tubular allotrope of carbon with graphitic structures (Figure 1.3). They can be classified into two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).\textsuperscript{17} CNTs have attracted significant interest in recent years for developing high-performance flexible SCs due to their high electrical conductivity, unique pore structure and good mechanical stability.\textsuperscript{18} CNTs possess moderate specific surface area compared to activated carbons, however, comparable specific capacitance values have been reported. Niu \textit{et al.} reported a MWCNT based electrode that exhibited a maximum specific capacitance of \(~110\) F g\textsuperscript{-1}.\textsuperscript{19} SWCNT based electrodes achieved a specific capacitance of as high as 180 F g\textsuperscript{-1}.\textsuperscript{20} Recent studies have shown that aligned CNTs are more efficient in ion transportation compared to randomly entangled CNT
structures. A high specific capacitance of 365 F g\(^{-1}\) has been obtained for a MWCNT array based electrode. \[21\]

![SWCNT and MWCNT](image)

Figure 1.3 Schematic structures of SWCNT and MWCNT. Reproduced with permission \[22\]. Copyright 2013, SAGE Publications.

Graphene, a one-atom thick single layer graphitic carbon (Figure 1.4), has also attracted significant attention as an electrode material for flexible SCs due to its high electrical properties, large surface area and high mechanical strength.\[23–26\] The theoretical specific surface area of pure graphene is about 2630 m\(^2\) g\(^{-1}\) \[27\], leading to the theoretical double-layer capacitance of 550 F g\(^{-1}\)\[28\]. However, this high level of capacitance is difficult to achieve as graphene sheets tend to restack during electrode preparation processes. Stoller and co-workers investigated reduced graphene oxide as an electrode material.\[27\] In the reported work, individual graphene sheets partially agglomerated during the reduction process, leading to moderate specific capacitances of 135 F g\(^{-1}\) and 99 F g\(^{-1}\) in aqueous and organic electrolytes, respectively. Zhu \textit{et al.} reported that KOH activated graphene
with pores could achieve a higher specific surface area of up to 3100 m$^2$ g$^{-1}$, resulting in a specific capacitance of 166 F g$^{-1}$ at a current density of 5.7 A g$^{-1}$.[29]

![Figure 1.4 Schematic structure of one single-layer graphene. Reproduced with permission[30]. Copyright 2012, the Royal Society of Chemistry.](image)

1.2.1.2 **Conducting polymers**

Conducting polymers (CPs) are organic polymers that can conduct electricity. In 2000, the Nobel Prize in Chemistry was awarded to Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa for their outstanding work on the conducting polymer polyacetylene.[31] During the past decades, numerous CPs have been developed, and found widespread application in polymer light-emitting diodes[32], sensors[33], artificial muscles[34], anticorrosion coatings[35], and energy conversion and storage devices[9,36]. CPs are suitable as electrode materials for flexible SCs as they possess many advantages: such as low cost, environmental friendliness, high conductivity in the doped state, high capacitance, ease of synthesis, and capability of manufacturing as self-supporting and flexible thin films.[9,37–40] The most commonly studied CPs in the field of SCs are polypyrrole (PPy)[41], polyaniline (PANi)[39], and derivatives of polythiophene (PTh), such as poly
(ethylenedioxythiophene) (PEDOT) \[^{42}\]. The structures of the common CPs are shown in Figure 1.5.

![Chemical structures of PPy, PANi, PTh and PEDOT (undoped form).](image)

Figure 1.5 Chemical structures of PPy, PANi, PTh and PEDOT (undoped form).

CPs can be p-doped (with anions) or n-doped (with cations). Electrochemical p-doping of conducting polymer occurs by removing electrons from the polymer chain and the addition of anions to the polymer backbone to balance the positive charge. The reverse mechanism (\(i.e.,\) the addition of electrons to the backbone and balancing the negative charge with cations) accounts for the electrochemical n-doping of conducting polymers. PPy and PANi can only be p-doped in supercapacitor systems due to the highly negative potentials required for n-doping, which are beyond the reduction potential limit of the electrolyte \[^{43}\]. PTh and its derivatives can be both p- and n-doped.\[^{44,45}\]
Electrodes made from CPs showed much higher specific capacitances compared to carbon materials. Fan et al. prepared a highly porous PPy electrode on Ti foil using the cyclic voltammetry method.\cite{46} The resultant PPy showed a specific capacitance of about 450 F g\(^{-1}\). PPy doped with Nafion ions or perchlorate exhibited a specific capacitance of 344 or 355 F g\(^{-1}\), respectively.\cite{47} PANi was reported to show a specific capacitance of more than 500 F g\(^{-1}\).\cite{48-58} A derivative of PTh, poly(tris(4-(thiophen-2-yl)phenyl)amine), can even achieve a specific capacitance greater than 990 F g\(^{-1}\).\cite{59} The drawback of CP based electrodes is that they suffer from structural degradation caused by swelling and shrinking of CPs during long term cycling, leading to a decay in their electrochemical performance. It is suggested that electrodes prepared from nanostructured CPs\cite{60} or composites of CPs with carbon based materials\cite{61-63} can show superior cyclic stabilities.

1.2.1.3 Composite materials

Carbon materials, such as CNTs and graphene, can be employed as a conducting substrate for the integration of pseudocapacitive materials to boost the electrode performance.\cite{64} The combination of carbon materials with conducting polymers has been proven to be effective for preparing electrodes for SCs due to the synergistic effect of electrochemical double-layer capacitance and pseudocapacitance.\cite{65} This strategy endows the CPs with improved cyclic stabilities as carbon materials such as CNTs and graphene, can act as frameworks to stabilize the CPs, limiting their swelling and shrinking during operating cycles.\cite{66} Apart from the CPs such as PPy\cite{67,68}, PANi\cite{69,70}, and PEDOT\cite{71}, various metal oxides, including MnO\(_x\)\cite{72,73}, RuO\(_2\)\cite{74}, V\(_2\)O\(_5\)\cite{75}, and Co\(_3\)O\(_4\)\cite{76} have also been explored for the fabrication of flexible carbon based composite electrodes.
1.2.2 Solid-state electrolytes

The use of solid-state electrolytes addresses the electrolyte leakage issue, and also facilitates simplifier device packaging processes. The most widely used solid-state electrolytes in SCs are polymer electrolytes. The ideal polymer electrolyte should be of high ionic conductivity at room temperature, low electronic conductivity and display good mechanical stability. Polymer electrolytes typically achieve their ionic conductivity through the movement of protons, lithium ions, or the ionic species in ionic liquids.[77]

Proton-conducting polymer electrolytes, composed of acid/polymer blends are the most widely used solid electrolytes for flexible SCs. The main polymer used in this system is poly (vinyl alcohol) (PVA), with H$_2$SO$_4$ and H$_3$PO$_4$ often chosen as the proton conductors.[67,78–80] This type of polymer electrolyte is typically prepared by the addition of an acid to the aqueous polymer solution. Free-standing electrolyte films can then be obtained by evaporating the water, and exhibit conductivities in the range of 10$^{-6}$-10$^{-3}$ S cm$^{-1}$. During the cell assembly process, the electrodes are either immersed in a hot polymer electrolyte solution or the electrolyte solution is cast on the electrode surface. The polymer electrolyte solution can penetrate the active layer of the electrodes, increasing the electrochemically active surface area.[77] After drying, two electrodes with polymer electrolyte are pressed face-to-face to form an integrated cell. Proton-conducting polymer electrolytes exhibit the highest conductivity among all polymer electrolytes. They can be prepared and used under ambient conditions and the presence of water helps to maintain high conductivity. However, their main drawback is the relatively narrow voltage window (usually limited to 1 V) of operation.[77]
Lithium ion-conducting polymer electrolytes are generally prepared by mixing a polymer, such as poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA) or poly(vinylidene fluoride) (PVDF) with a lithium salt dissolved in an organic solvent. Solvents such as ethylene carbonate (EC), propylene carbonate (PC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), dimethyl formamide (DMF) and tetrahydrofuran (THF) have been found to also act as a plasticizer giving rise to a higher conductivity [81]. Lithium ion-conducting polymer electrolytes are prepared by dissolving various lithium salts in organic solvents and immobilizing them in a polymer matrix. Lithium ion based solid electrolytes can operate in a wide electrochemical window. However, they are moisture sensitive and require both an oxygen and moisture free environment for successful cell assembly.

Ionic liquids are a class of liquid salts. Their unique properties, such as low volatility and low flammability, high thermal stability and wide potential window, make them suitable electrolytes for supercapacitor applications [82]. They can be trapped in a polymer matrix or a silica network, forming an ion gel that can be used as a solid electrolyte [83–86].

1.2.3 Device architecture of flexible supercapacitor

The electrochemical performance of a supercapacitor, is dependent not only on the properties of the materials used in each component, but also on how these components are designed, matched and combined to form a device that can satisfy the target performance requirements. Discussed below are two widely studied architectures used for flexible supercapacitor (fSC) devices: sandwiched stacked structure and interdigitated planar structure [87–89] (Figure 1.6).
Figure 1.6 Schematic diagrams of flexible SCs with (a) conventional sandwiched structure and (b) interdigitated structure.

Early all-solid-state fSCs adopted the conventional sandwiched structure design with a stacked configuration of current collector/film electrode/solid electrolyte/film electrode/current collector (Figure 1.6a). This design attracted the attention of researchers due to its extremely simple structure and relatively easy fabrication process. However, when thicker electrodes are required, this design often suffers from serious ion transport limitations due to the consequently increased ion transport path\cite{87,90}. Moreover, portable electronic devices should not only be flexible, but also need to be small in both overall size and thickness. Bulky sandwiched architectures are not compatible with the planar geometries of miniaturized micro-electronics and are not suitable for electronic circuitry.\cite{87}

To overcome this challenge, a planar design with several microelectrodes (as each electrode) interdigitally arranged on a flexible substrate such as terephthalate (PET) or polyimide (PI) films or papers (interdigitated design), was developed as a new emerging device structure (Figure 1.6b).\cite{87} The fabrication of interdigitated microelectrodes often involves an additional micro-patterning step before or after film electrode deposition. Compared with the stacked sandwiched structure, the planar interdigitated structure possesses the following advantages:
• Space-saving device. Without a layer of solid electrolyte used as a separator in the sandwiched design, the interdigitated fSC device is thinner and less in volume and can store and provide more power in a limited space without the volume being wasted on the separator layer.

• Shorter ion transport paths. Advances in micro-patterning techniques make it possible to accurately control very small distances between adjacent electrodes thereby shortening the ion transport path. This results in decreasing the ion transport resistance, increasing the rate capability and power density of the device.

• Better penetration of electrolyte ions. The increased exposure of the microelectrodes to the electrolyte in the interdigitated design can increase the ion accessibility of the inner surface of the electrode materials resulting in improved energy storage.

• Facile interconnection and integration within electronic systems. Most applications require a current or voltage that is higher than what can be delivered by a single SC device. Hence, the connection of the SC devices in series, parallel or a combination of both is needed. Having the electrodes in the same plane would facilitate these connections on one chip, avoiding intricate wired interconnections between sandwiched SCs.[91]

The drawbacks of the interdigitated design are as follows:

• Less areal energy. The footprint area of the interdigitated SCs includes the active surface areas of both electrodes and an inactive gap surface in between, while the
footprint area of the sandwiched SCs is only defined by the active materials. Hence, a higher areal energy can be achieved for SCs in the sandwiched configuration. The adverse impact of the interdigitated SCs can be minimized by decreasing the distance between the adjacent electrodes. However, it normally involves more expensive micro-fabrication techniques with fine control on resolution.

- Additional consumption of expenses and labour in the patterning step. This is the main challenge for the scale-up of the interdigitated design for commercial applications. Efforts are being devoted to developing scalable micro-fabrication techniques for various electrode materials, which will be discussed in section 1.3.2.

Sandwiched SCs are still the industrially favored device design due to their facile and low-cost fabrication process, although the interdigitated structures show many advantages. However, with the development of miniaturized wearable electronics and the continuous progress in micro-patterning techniques, interdigitated SCs may find an increased application.

### 1.3 Film electrodes for flexible SCs with sandwiched structure.

The major challenge of the fabrication of sandwiched structured SCs is to prepare flexible electrodes with both robust mechanical properties and superior electrochemical performance. To make the electrode flexible, flexible substrates (like PET film, PDMS, papers, or textiles) have been used to act as the mechanical support for rigid active materials. Free-standing films comprising active materials have also been fabricated based on robust and flexible active materials, like CNTs and graphene.
1.3.1 Substrate-supported flexible electrodes.

1.3.1.1 Flat substrate

Mechanically flexible, thin and lightweight plastics such as polyethylene terephthalate (PET) have been widely used as the supporting substrates for flexible SCs. Kaempgen et al. [92] demonstrated a thin film supercapacitor based on spray coated SWCNT networks (served as both electrode and current collector) on a PET substrate using a PVA/H$_3$PO$_4$ gel electrolyte (Figure 1.7a-b). The SWCNT network showed a specific capacitance of ~36 F g$^{-1}$ in the solid-state device. Chen et al. reported a ultrathin (25 nm of film thickness) and transparent (70% transmittance) graphene film, which was vacuum filtrated and transferred on PET substrate for use in a supercapacitor, which showed a specific capacitance of 135 F g$^{-1}$ at a current density of 0.75 A g$^{-1}$. [93]

Figure 1.7 (a) SEM image of the SWCNT network. (b) Photograph of a SWCNT network based flexible supercapacitor. Reproduced with permission [92]. Copyright 2009, American Chemical Society.
1.3.1.2 *Porous substrates*

Porous sheets, such as paper\textsuperscript{[94]}, textile\textsuperscript{[95]} and sponges\textsuperscript{[96]}, are better substrate candidates than PET. They can not only provide flexible support, but also offer higher surface area for active materials. Various types of materials, including carbon materials (carbon nanotubes\textsuperscript{[97]}, graphene\textsuperscript{[98]} etc.), conducting polymers (PANI\textsuperscript{[94]}, Ppy\textsuperscript{[99]} etc.), metal oxides (RuO\textsubscript{2}\textsuperscript{[74]}, MnO\textsubscript{2}\textsuperscript{[100]}, and VO\textsubscript{x}\textsuperscript{[101]} etc.) and composites of these materials, have been coated or grown on these porous and flexible substrates via different methods like dip-coating\textsuperscript{[96,102,103]}, chemical\textsuperscript{[99]} or electrochemical deposition\textsuperscript{[94,104]} etc.

Yao \textit{et al.}\textsuperscript{[105]} introduced a pencil-drawing and a subsequent PANi electrodeposition to fabricate graphite/PANI hybrid electrodes on a paper substrate. The hybrid electrode was made by first drawing a conductive graphite layer on paper using a pencil. Electrochemical deposition of PANi nanowire networks was then carried out on the graphite layer. The solid-state supercapacitor was assembled by two graphite/PANI electrodes sandwiching a PVA/H\textsubscript{2}SO\textsubscript{4} electrolyte layer and achieved a high energy density of 0.31 mWh cm\textsuperscript{-3} at a power density of 0.054 W cm\textsuperscript{-1}. Liu \textit{et al.}\textsuperscript{[106]} demonstrated a PANi-rGO-cellulose paper nanocomposite electrode. The fabrication of nanocomposite electrodes started with dip-coating a GO layer on the cellulose fibres in the paper. The GO coated cellulose fibre paper was then used as a template to assemble porous rGO networks in the pores of the paper by a hydrothermal process. PANi was then chemically polymerized onto the rGO-paper to obtain PANi-rGO/paper composite paper (Figure 1.8a). A solid-state supercapacitor was assembled by sandwiching two such composite paper with PVA/H\textsubscript{2}SO\textsubscript{4} polymer electrolyte (Figure 1.8b). The calculated specific
capacitance of PANi-rGO/paper electrode was about 224 F g$^{-1}$, and the solid-state device showed stable performance at folding and bending states (Figure 1.8c).

Figure 1.8 (a) Schematic diagram of the preparation of the PANi-rGO/cellulose fibre composite paper. (b) Schematic diagram of an all-solid-state integrated supercapacitor device. (c) CV curves of the all-solid-state supercapacitor under different deformation conditions (scan rate: 2 mV s$^{-1}$). Reproduced with permission$^{[106]}$. Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Textiles have hierarchical porosity in their fibres and yarns, and there is also free space between fibres and yarns. Such inherently porous structures facilitate the accommodation of active materials. Yun et al. $^{[95]}$ designed a solid-state stretchable textile supercapacitor using PPy-MnO$_2$/CNT coated textile electrodes and a PEO based gel electrolyte. A piece of textile made of cotton was dipped into SWCNT ink to obtain a conductive textile, MnO$_2$ and PPy was then electrodeposited on the SWCNT coated textile. The textile
supercapacitor exhibited excellent energy and power densities of 31.1 Wh kg\(^{-1}\) and 22.1 kW kg\(^{-1}\), respectively. The textile device showed a stable electrochemical performance under bending and stretching deformations. Highly conductive carbon cloths were also employed as substrates as an alternative for flexible textile supercapacitor fabrication. For instance, Yuan et al. \cite{107} fabricated a solid-state supercapacitor using a carbon cloth as a current collector and mechanical support for the carbon nanoparticles/MnO\(_2\) nanorods hybrid electrode and PVA/H\(_3\)PO\(_4\) electrolyte (Figure 1.9a). The device showed a high energy density of 4.8 Wh kg\(^{-1}\) at a power density of 14 kW kg\(^{-1}\). The device could be bented without sacrificing its performance (Figure 1.9b).

Figure 1.9 (a) Photographs of the solid-state supercapacitor made of carbon nanoparticles/MnO\(_2\) nanorods hybrid electrode and a carbon cloth at normal, bent and twisted state. The image on the right shows a red LED turned on by three SCs connected in series. (b) CV curves for the solid-state supercapacitor at different bending angles. Reproduced from reference\cite{107} with permission. Copyright 2012, American Chemical Society.
1.3.2 Free-standing flexible electrodes

Despite the use of a carrier substrate as a simple and effective strategy to enable fabrication of flexible electrodes, the drawbacks are also obvious. The electric and electrochemical inert substrate increases the total weight of the whole device, which is not desirable for use in wearable applications. Meanwhile, the attachment between substrate and active materials can also deteriorate or be affected during electrochemical cycles and repeated deformation. Therefore, it is still important to develop free-standing and intrinsically flexible film electrodes, in which the full electrode structure is fully utilized. CNT and graphene are two main types of active materials, which have the potential to be fabricated into free-standing film electrodes due to their intrinsic mechanical strength. In addition, other active materials including conducting polymers and metal oxides, can be incorporated into flexible carbon backbones with high electrical conductivity and large surface area.

1.3.2.1 Carbon nanotube-based electrodes

CNTs can be assembled into freestanding films through chemical vapour deposition (CVD) methods and vacuum filtration-induced self-assembly. The free-standing film developed from a floating catalyst CVD technique exhibits high tensile strength of 360 MPa and electrical conductivity of 2000 S cm\(^{-1}\).\(^{[108]}\) These CNT films were modified and utilized as electrode materials for flexible SCs by Niu et al, and exhibit an electrode capacitance of 35 F g\(^{-1}\).\(^{[109]}\) Free-standing CNT films can also be obtained by vacuum filtration. In a typical process, a stable CNT dispersion is first formed by breaking up large bundles of CNTs in water (with the aid of a surfactant) or in organic solvents using ultrasonic energy. During the filtration process, CNTs are trapped inside or on the surface
of the membrane pores, forming an interconnected and entangled film. The CNT film can then be peeled off after sufficient film thickness has been achieved.\cite{110}

Pseudo-capacitive materials (PANi,\cite{80,111} MnO\textsubscript{2},\cite{112} PEDOT\cite{113}) can be directly chemically or electrochemically deposited on the free-standing CNT films or mixed with CNTs in dispersion prior to the vacuum filtration film forming process. The specific capacitance can be greatly improved with the incorporated pseudo-capacitive materials. For example, Meng et al. developed a solid-state paper-like supercapacitor based on PANi coated free standing CNT film and PVA/H\textsubscript{2}SO\textsubscript{4} gel electrolyte (Figure 1.10a).\cite{80} PANi can be uniformly coated around the surface of CNTs and their bundles via \textit{in situ} chemical polymerization method. The framework of the porous CNT networks was maintained after PANi coating, which provides superior mechanical property of flexibility for the electrodes and extremely large surface area of electrode/electrolyte interface. This device showed a specific capacitance of 350 F g\textsuperscript{-1}, excellent cycling stability, and unaffected electrochemical performance under flexible state (Figure 1.10b).
Figure 1.10 (a) Schematic illustration of the PANI/CNT nanocomposite electrodes well solidified in the polymer gel electrolyte. (b) CV curves of the all-solid-state device (size~0.5 cm × 2.0 cm) under normal condition, and its highly flexible (twisting and folded). Reproduced from reference [114] with permission. Copyright 2012, American Chemical Society.

1.3.2.2 Graphene-based electrodes

Freestanding graphene films or papers, have also shown great promise as flexible electrodes for SCs as they are ultrathin, flexible and lightweight. Graphene films have been fabricated through various solution processing methods, such as vacuum filtration, spin-coating, Langmuir-Blodgett, layer-by-layer deposition and interfacial self-assembly.[115] However, during the fabrication process, graphene sheets tend to aggregate and restack due to strong π − π interactions and van der Waals forces, limiting the
available surface area and the diffusion of electrolyte ions, resulting in deteriorating electrochemical performance. To prevent the restacking of graphene sheets, two main strategies have been proposed: 1) add spaces such as CNTs, and polymers [116–118], and 2) produce 3D porous graphene networks [119,120].

Shi et al. [117] fabricated a flexible electrode from reduced graphene oxide (rGO) /poly (vinyl pyrrolidone) (PVP) composite film (Figure 1.11 a and b). The PVP chains were found to effectively intercalate between the graphene sheets, acting as spacers to prevent the graphene sheets restacking. The composite films showed a high mechanical strength of ~121.5 MPa (Figure 1.11c). The solid-state SCs based on the rGO/PVP composite containing 55% rGO (by weight) showed high volumetric specific capacitances (67.4 F cm⁻³ at 1 A g⁻¹), good rate-capability (51.4 F cm⁻³ at 100 A g⁻¹), and excellent flexibility (Figure 1.11d). Park et al. [118] prepared Nafion functionalized rGO films using a supramolecular assembly approach and vacuum filtration. The integration of Nafion not only prevented the restacking of graphene sheets, but also improved the interfacial wettability between the electrodes and electrolyte. All-solid-state SCs were fabricated by sandwiching Nafion membranes between the functionalized rGO thin films. The specific capacitance of functionalized rGO was 118.5 F g⁻¹, which is about two times higher than the reported value for the pure rGO (62.3 F g⁻¹). After bending at a radius of 2.2 mm, cyclic voltammetry (CV) curves of the supercapacitor exhibited almost the same shape as those in the flat state, indicating the high mechanical stability.
Figure 1.11 (a) Schematic illustration of fabrication of rGO/PVP composite film and the diffusion of the electrolyte onto the surfaces of rGO sheets. (b) Photograph and (c) tensile stress-strain property of the flexible rGO/PVP film. (d) CV curves of the solid-state device based on the rGO_{55}/PVP_{45} composite film with a thickness of 2.4 μm in various bending states (scan rate = 100 mV s\(^{-1}\)). Reproduced with permission \(^{[117]}\). Copyright 2014, the Royal Society of Chemistry.

Tremendous attention has also been paid to 3D porous graphene networks to prevent the aggregation of the graphene sheets. The general network preparation approaches involved include freeze drying \(^{[121]}\), hydrothermal \(^{[119]}\), and organic sol-gel \(^{[122]}\). Shu \textit{et al.}\(^{[120]}\) prepared a flexible free standing 3D graphene with interconnected porous structure by freeze drying a wet GO gel, followed by thermal and chemical reduction (Figure 1.12a). The water in the precursor GO gel helped to prevent the restacking of the graphene sheets.
The porous graphene paper was highly flexible (Figure 1.12b). A flexible solid-state supercapacitor was fabricated using those graphene papers and PVA/H\textsubscript{2}SO\textsubscript{4} polymer electrolyte (Figure 1.12 c and d). The graphene paper in the device delivered a specific capacitance of 137 F g\textsuperscript{-1} at 1 A g\textsuperscript{-1} and it can maintain 94\% of its capacitance under bending (Figure 1.12e). 3D graphene macrostructures such as graphene hydrogels can also be prepared by a one-step hydrothermal process. Xu et al. \cite{119} pressed the hydrothermally reduced graphene hydrogel onto gold coated polyimide substrate with a PVA/H\textsubscript{2}SO\textsubscript{4} polymer electrolyte to assemble flexible solid-state SCs. The graphene gel film in the solid-state device achieved a high specific capacitance of 186 F g\textsuperscript{-1} at 1A g\textsuperscript{-1}, and the device showed stable electrochemical performance under a range of bending angles.

Pseudo-capacitive materials can also act as spacers of graphene sheets, which not only prevent the re-stacking problem, but also offer high capacitance. A flexible and conductive composite film of chemically converted graphene (CCG) and polyaniline nanofibers (PANi-NFs) were prepared by vacuum filtration of a mixed dispersion of both components\cite{70}. It was found that the PANi-NFs are sandwiched between layered CCGs and produced a porous film. The composite film with 30 wt.\% CCG exhibit an improved specific capacitance of 210 F g\textsuperscript{-1} compared with that of the CCG electrode (57 F g\textsuperscript{-1}) when assembled into sandwiched supercapacitor devices. Li et al. reported a graphene/MnO\textsubscript{2} composite film using the \textit{in situ} grown MnO\textsubscript{2} nanoparticles decorated graphene oxide as precursor. The film with MnO\textsubscript{2} weight ratio of 24\% can deliver a specific capacitance of 256 F g\textsuperscript{-1} at a current density of 500 mA g\textsuperscript{-1}\cite{123}. These reports showed the excellent synergistic effect between graphene and pseudo-capacitive materials in pursuing high performance flexible SCs.
Figure 1.12 (a) Cross-sectional SEM image of a porous graphene paper. (b) Photograph of the porous graphene paper demonstrating its flexibility. (c) Schematic procedure to fabricate a solid-state supercapacitor from the porous graphene paper. (d) Photograph of the flexible device at a bending state. (e) CV curves of the flexible device at bending and relaxation state (scan rate = 10 mV s\(^{-1}\)). Reproduced with permission\[^{124}\]. Copyright 2015, the Royal Society of Chemistry.

1.4 Patterned electrodes for flexible microsupercapacitor with interdigitated structure

The fabrication of flexible micro-SCs with interdigitated design involves a micro-patterning step before or after the flexible film electrode formation. Recent developments
in micro-manufacturing technology have opened pathways for the patterning step of the micro-supercapacitor fabrication that suit the type of active materials and the required performance (either high energy density or high power density). The fabrication methods can be mainly classified into three categories: \textit{in situ} synthesis of active materials on a pre-patterned surface, patterning the well-developed film electrode, and directly printing of existing active materials.

\textbf{1.4.1 In-situ synthesis of active materials on pre-patterned surfaces}

Active materials can be synthesized on a pre-patterned surface via various synthesis techniques (such as electrochemical polymerization\cite{125,126}, electrolytic deposition\cite{127,128}, electrophoretic deposition\cite{91}, chemical deposition\cite{129}, \textit{etc.}). Here, a pre-patterned surface is first prepared by coating and patterning a thin layer of photoresist (PR) or removable ink on a flexible substrate. In the next step, the current collectors are coated on the flexible substrate using the patterned PR or ink as a mask followed by the deposition of the active material. The masks are chemically removed either before or after the active materials deposition, when they are no longer needed.

\textit{1.4.1.1 Photolithography}

Sung \textit{et al.} \cite{125} reported a PR patterning method using the conventional photolithography technique which was the earliest and the most common method of mask preparation for the current collector coating. In this approach, a patterned interdigitated gold micro-electrode pair were first prepared on a silicon wafer by photolithography. PPy was then electrochemically polymerized on the pre-patterned gold layer. In the next step, a layer of solidified PVA-H$_3$PO$_4$ gel electrolyte was firmly attached to the PPy
microelectrode arrays. Upon detaching both PPy and the electrolyte layer from the silicon substrate, a small, lightweight, free-standing and flexible microsupercapacitor (fMSC) device was achieved. A relatively poor electrochemical performance (with areal capacitance of the device < 0.5 mF cm\(^{-2}\)) was observed for this fMSC device. This poor performance emanated from the primitive device assembly technique, with a lack of current collectors, and inappropriate coating of the electrolyte (simply attaching the dried gel electrolyte film to the electrode materials). Nevertheless, this study demonstrated the feasibility of fabricating flexible all-solid-state microsupercapacitor devices.

Using similar techniques (photolithography and \textit{in situ} chemical polymerization), Wang \textit{et al.} \cite{129} further modified and improved the fabrication steps of fMSCs (Figure 1.13). They directly prepared PANi based micro-electrodes with Au/Cr as the current collector on a flexible PET film as the substrate. Moreover, instead of attaching a layer of the solidified electrolyte on active materials, the PVA-H\(_2\)SO\(_4\) gel electrolyte was drop-cast on the surface of the microelectrodes and then solidified. Taking advantage of the advanced nanostructure of PANi electrodes, existence of current collectors, and better penetration of the electrolyte, the as-prepared fMSCs exhibited an excellent device capacitance of 1.17 mF cm\(^{-2}\) and 25.4 F cm\(^{-3}\) (23.52 mF cm\(^{-2}\) and 588 F cm\(^{-3}\) for electrode materials), a high scan rate capability (>10 V s\(^{-1}\)), and a low leakage current. In addition, the feasibility of increasing the operating voltage and/or current by simply making series and/or parallel connecting circuits of MSC units on one PET film was demonstrated for the first time. This is important in industrial applications where the required voltage or current are typically higher than what one single fMSC can supply. Following this approach, additional conducting polymers, carbon materials such as rGO\cite{91}, CNT\cite{85}, and metal oxide\cite{130} based electrodes were also fabricated. Despite the high resolution of the
prepared interdigitated microelectrodes (minimum width of array ~50 µm) and the excellent fMSCs device performance, the high-cost and the sophisticated process of photolithography limited its further development towards commercialization.

![Fabrication process for interdigitated microelectrodes](image)

Figure 1.13 A Schematic of fabrication process for interdigitated microelectrodes of PANi nanowire arrays on a flexible film. Reproduced from ref [129] with permission. Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.4.1.2 **Ink and pen lithography**

Commercial and printable inks can also be used as the mask material instead of PR. Using a common office laser printer, Ye’s group has printed a circuit template as a mask on a PET film.[126,128] They deposited Au/PANi and Au/MnO2/Au (AMA) stacked microelectrodes respectively on the mask by beam evaporation of Au current collectors and the electrodeposition of the active materials (Figure 15a-g). The fMSC devices were achieved by lifting off the printed circuit template using tetrahydrofuran. As the circuit pattern can be designed on a personal computer using software, the dimension parameters and the number of patterns could be easily adjusted. Hundreds of patterns can be printed
on a flexible PET film (Figure 15h, i) indicating the great potential of this approach for scalable fMSC fabrication. Jiang et al. used a Marker Pen Lithography technique, in which sacrificial ink patterns were written using commercial marker pens on substrate and were used as the mask for the deposition of current collectors and active materials (PEDOT and PANi).\textsuperscript{[131]} Despite the relatively low feature resolution which inhibits performance (minimum printed line width >250 µm for laser printer, ~500 µm for maker pen), the simplicity of these innovative strategies opened up new avenues for easy and scalable fabrication of fMSCs.

Figure 1.14 (a-g) Schematic illustrations of the fabrication procedure for the on-chip fMSCs with AMA stacked hybrid electrodes and single AMA sandwich hybrid electrode units. (h) a photograph of a large area of printed interdigitated patterns on a flexible PET film. (i) a photograph of the as-prepared on-chip fMSCs with AMA stacked hybrid
The fMSCs prepared from pseudo-capacitive electrode materials showed superior areal and volumetric capacitances (9-41 mF cm\(^{-2}\) and 50-147 F cm\(^{-3}\) respectively) compared to the relatively low capacitance of the carbon-based fMSCs (<1 mF cm\(^{-2}\) and <20 F cm\(^{-3}\) respectively) normalized by the area and volume of the whole device. The poor performance of carbon-based devices can be explained by the ultrathin thickness (~25 nm~1 µm) of the \textit{in situ} synthesized active materials, as carbon-based materials have poorer adhesion to the current collectors and substrates than pseudo-capacitive materials. Meanwhile, the relatively low intrinsic volumetric capacitance exacerbates the poor areal capacitance of the ultrathin carbon-based device\(^{[90]}\). Also, some of the techniques used for the \textit{in situ} deposition of carbon materials (such as electrostatic spray deposition of GO/CNT\(^{[132]}\), chemical vapor deposition of graphene\(^{[133]}\) and CNT\(^{[134]}\), etc.) require stringent conditions, \textit{e.g.}, relatively high temperature, that may not be compatible with the commonly used low-cost PET and paper substrates used in fMSC fabrication. In addition, post-processing by carefully and fully removing PR residue or ink masks is labour-intensive and may result in loss of some of the active materials. These limitations motivated the search for alternative ways for the preparation of carbon-based fMSCs.

\textbf{1.4.2 Patterning of well-developed film electrodes}

Patterning the pre-prepared film electrodes using techniques such as selective etching or converting is another approach to develop interdigitated fMSC devices. Active materials used in this category can be carbon materials, conducting polymers, metal oxides, and a
combination of those. Methods for patterning of film electrodes are classified into mask/template patterning and mask-free patterning processes.

1.4.2.1 Oxygen plasma etching

Plasma etching is a conventionally used dry-etching method for mask preparation. Electrode films are first prepared directly or transferred to a desired flexible substrate via one of the film formation methods (such as spin coating and vacuum filtration). A thin layer of a current collector (e.g., Au) is then coated on the film with a customized mask. Films with the patterned current collector coatings are irradiated in a plasma chamber and the exposed part of electrode materials was etched to form interdigitated electrodes. This method has been used to develop high performance electrode films (e.g. graphene\textsuperscript{[135]}, graphene/polyaniline\textsuperscript{[136]}, graphene/MnO\textsubscript{2}/Ag nanowires\textsuperscript{[137]}, NiFe\textsubscript{2}O\textsubscript{4} nanofibers\textsuperscript{[138]}) for fMSCs. In another study, alternating stacked graphene/PANi films were prepared by layer-by-layer vacuum filtration\textsuperscript{[136]}. As shown in Figure 1.15, the 2D pseudocapacitive graphene-conducting polymer nanosheets (PANi-G) and electrochemically exfoliated graphene (EG) were alternately and densely stacked layer by layer. The mesoporous PANi-G with easily accessible ion-transporting channels acts as a pseudocapacitance and highly conductive EG provides an electron-conducting network for rapid electron transport. Coupled with an interdigitated architecture, the fabricated fMSC exhibited an extremely high device areal capacitance of \(~52.5\) mF cm\textsuperscript{-2} and volumetric capacitance of \(~109\) F cm\textsuperscript{-3}. 

34
1.4.2.2 Microfluidic etching

Xue et al. used a microfluidic etching method, in which a patterned poly(dimethylsiloxane) (PDMS) elastomer stamp acted as the template for etching\textsuperscript{[139]}. The PDMS stamp was impressed onto an electrospun MnO\textsubscript{2} film, and then different aqueous etching solutions were passed from the microfluidic channels to etch the MnO\textsubscript{2} resulting in interdigitated microelectrodes. The PDMS stamp is cheap and stable against most etchants that react with a variety of active materials, making microfluidic etching a versatile and low-cost way for electrode patterning. Both of the above etching methods rely on masks or templates for the development of the desired patterns, which are labour
intensive and difficult to adjust the patterning parameters for commercial applications.
To solve these problems, mask-free patterning methods have been gradually emerged.

1.4.2.3 Laser writing

The application of laser for direct writing of graphene-based fMSCs was reported by several groups and has shown great potential for commercialization.\cite{83,140,141} In this method, thin films of graphene precursors (graphene oxide and commercialized polyimide sheets) are selectively converted and patterned to graphene interdigitated microelectrodes using a laser system. For example, El-Kady et al. described a scalable fabrication method for graphene fMSCs by direct laser writing on GO films using a standard LightScribe DVD burner (Figure 1.16).\cite{142} By this means, more than 100 MSCs could be readily generated on a single disc in ~30 min. Dimensions of the interdigitated micro-fingers were adjusted to control the energy and power handling. Considering lasers’ wide application in industry for metal cutting and welding, and the wide range of wavelengths and powers that are available, laser patterning is a promising tool to fabricate fMSCs at scale. However, the areal capacitances of laser-patterned graphene fMSCs were relatively low, only 1-16 mF cm$^{-2}$. The reason for the low capacitance of the fMSCs may be due to the conversion of graphene only being performed on the surface of the graphene precursor thin-films, limiting its applicability for thick films. Also, the residual precursor of graphene left between the fingers would not only reduce the ion diffusion rate but also affect the penetration of electrolyte ions from the lateral side of microelectrodes for increasing film thicknesses. In addition, this technique has only been reported for graphene-based fMSCs and may not be applicable to other active materials.
1.4.2.4 Laser-etching

Recently, the laser lithography technology (known as laser-cutting) has been used as an etching tool to create patterned channels on various kinds of film electrodes such as MoS$_2$, activated mesophase pitch (aMP), mushroom-derived carbon (MDC), and MXene ($\text{Ti}_3\text{C}_2\text{Tx}$). This laser cutting approach “etches” unwanted material away from the electrode as opposed to “writing” the electrode to generate patterned electrode design on the substrate (Figure 19). Teng et al. applied laser-etching on an aMP electrode film (~5 $\mu$m thickness) to generate interdigitated patterns (electrode width of ~350 $\mu$m and interspace between electrodes ~150 $\mu$m). The fabricated fMSC exhibit an areal capacitance of ~8.4 mF cm$^{-2}$ and had a volumetric capacitance of ~12 F cm$^{-3}$ based on the
area and volume of the whole device. Higher capacitances of 27 mF cm\(^{-2}\) and 337 F cm\(^{-3}\) were achieved by an all-Mxene-based fMSC, in which the \(\sim 1\ \mu m\) Mxene layer was laser-etched into interdigitated patterns.\(^{146}\) It is believed that this technology can be applied to a wide range of electrode materials and film thicknesses provided that residual precursors (or any unwanted materials) can be completely removed to create well-separated microelectrodes. The simplicity of this technology (\textit{i.e.}, computer-generated intricate patterns that can be “written” on any material such as polymers, nanomaterials, and many others on the desired substrates with complex shapes and structures) can pave the way for rational engineering of novel materials suitable for a wide range of wearable electronic devices not limited to energy storage applications.

To conclude, patterning on pre-developed film is an effective way to maintain the structures of electrode materials containing single or multi components, among which laser etching shows its simplicity and scalability compared to other techniques. However, the significant waste of materials (\textit{i.e.} etched and unused materials) and the limitation on producing only symmetric fMSCs restrict the further application of this technique in fabricating fMSC electrodes.
Figure 1.17 Schematic diagram of the process used in the fabrication of an all-solid-state MSC. The fabrication flow includes (a) evaporation deposition of an Au layer on the substrate, (b) construction of the aMP carbon film on the Au layer using EPD, (c) channel patterning on the carbon film using a CO$_2$-laser writer, and (d) drop-casting and solidification of a gel electrolyte on the interdigitated microelectrode. Reproduced from $^{[144]}$ with permission from Elsevier.

1.4.3 Direct printing of active materials
Direct printing of inks containing active materials onto a flexible substrate is another approach by which microelectrodes can be fabricated for use in fMSCs. Starting from carbon material powders, a stable suspension or a viscous slurry is first obtained. A binder, surfactant, and/or conductive additives may also be added to the suspension to improve the printability and/or conductivity of the active materials. Compared to the sophisticated steps required in the preparation of microelectrodes using the pre-patterning approach, the direct printing of the active materials can realize the deposition and patterning simultaneously in one step, thus reducing materials usage and process complexities. Different printing techniques (such as inkjet-printing \cite{147-149}, extrusion printing \cite{150}, screen printing \cite{151,152}, roll-to-roll printing \cite{153,154}, etc.) have been exploited to prepare patterned microelectrodes from carbonaceous materials to make fMSCs. Highly dispersed and stable active materials with suitable particle sizes and appropriate rheological properties are required for successful patterning using printing techniques.

1.4.3.1 Screen printing

In screen printing, the ink is forced through a screen with pre-patterned open meshes and then contacts the substrate (Figure 16a). Screen printing can be carried out in a large scale with uniform thickness and within a short period. It also allows for patterning on a variety of substrates, not only on a smooth plastic film, but also on a porous cloth and papers. Screen printing has enabled the integration of various composite active materials with
superior nanostructures into fMSCs, which were incompatible with other fabrication strategies. For instance, using screen printing techniques, Wang et al. fabricated a MnO$_2$/onion-like carbon (MnO$_2$/OLC)-based fMSC, in which the MnO$_2$/OLC nanocomposites have unique nano-urchin shapes with the diameter of 200-500 nm.$^{[155]}$ The optimized device exhibited high areal and volumetric capacitances of ~7.04 mF cm$^{-2}$ and ~7.04 F cm$^{-3}$. Similarly, Zhu et al. screen printed interdigitated electrodes using the ink of novel 3D nanocomposite which consisting of cobalt oxide (CoO) nanoflowers woven with CNTs networks.$^{[151]}$ High volumetric and areal capacitances of ~17.4 F cm$^{-3}$ and ~17.4 mF cm$^{-2}$ respectively, and a high energy density of ~3.48 mWh cm$^{-3}$ were achieved for the fMSC device. In another study, nitrogen-doped graphene was screen printed at a relatively high electrode thickness of ~10 µm achieving a high areal capacitance of ~3.4 mF cm$^{-2}$, that is much higher than the areal capacitance of carbon-based fMSCs prepared by the pre-patternning approach.$^{[152]}$

1.4.3.2 Gravure printing

Gravure printing is another fast printing technique for fMSC patterning, which is used traditionally for the roll-to-roll printing of newspapers, magazines and packages (Figure 16b). In this approach, an image or a pattern are carved into the surface of a cylinder, and then the inks are then transferred from the carved cells onto the substrate as a result of the high printing pressure and adhesive forces between the ink and substrate. Carbon materials (e.g., crumpled graphene) and nanostructured composite (e.g., hybrid MoS$_2$@S-rGO consisting of sulfonated reduced graphene oxide and MoS$_2$ nanoflowers) were gravure printed into microelectrode with the thickness of ~10 µm.$^{[153,154]}$ High areal capacitances of 6.65 mF cm$^{-2}$ and 6.56 mF cm$^{-2}$ have been achieved by these graphene
and MoS$_2$@S-rGO-based fMSCs, respectively. However, both screen printing and gravure printing use pre-patterned screens or cylinders making the adjustment of the patterning parameters difficult. Moreover, the resolution of ~300 µm for screen printing and ~700 µm for gravure printing are relatively poor, limiting the size and the performance of the final fMSC device. To circumvent these problems, digital printing technology, such as inkjet printing and extrusion printing, were used that have high pattern precision.

### 1.4.3.3 Ink-jet printing

Ink-jet printing is a digital, non-contact printing technology which provides precise control over patterns position through a moving $XY$ printing head and over the thickness of the printing (Figure 16c). Ink-jet printing allows printing on a variety of substrates using simple drawn patterns via softwares on a computer. Lee et al. used a GO ink and ink-jet printed a pair of 4-interdigitated patterns with dimensions of 1.75 mm $\times$ 1.89 mm with 80 µm spacings between the adjacent interdigitated fingers on a flexible PET film.$^{[148]}$ After the in-depth reduction of GO to graphene using a photo-thermal technique with a xenon flash camera, a porous graphene-based fMSC with a maximum volumetric capacitance of 0.82 F cm$^{-3}$ was obtained. Hersam et al. also used an ink-jet printer for the fabrication of graphene-based fMSCs from a printable and highly conductive graphene ink and achieved an improved volumetric capacitance (~9.3 F cm$^{-3}$) in the PVA/H$_3$PO$_4$ solid-electrolyte.$^{[156]}$ They demonstrated the scalable printing of well-defined patterns on a flexible polyimide film.

Asymmetric patterns can also be achieved by ink-jet printing different metal-based and carbon materials-based inks and be used for fabricating asymmetric fMSC devices. Pang
et al. made an asymmetric fMSC device for the first time by ink-jet printing lamellar potassium cobalt phosphate hydrate \([\text{K}_2\text{Co}_3(\text{P}_2\text{O}_7)\cdot2\text{H}_2\text{O}]\) nanocrystal whiskers dispersion as the ink for cathode and graphene as the ink for anode.\textsuperscript{[147]} The device with high pattern resolution (70 ~ 80 µm) delivered a volumetric capacitance of \(~6.0\ \text{F}\ cm^{-3}\) with a maximum volumetric energy density of \(~0.96\ \text{mWh}\ cm^{-3}\) in PVA/KOH electrolyte. They also printed silver inks as current collectors prior to the deposition of active materials and were able to improve the rate capability of fMSCs. In another study, an all ink-jet printed solid-state fMSC was fabricated using printable CNT active materials and UV curable gel electrolytes.\textsuperscript{[157]} This work opened up a new way for the fabrication of fMSCs and their application in next-generation fully-printed wearable electronics. The main challenge in ink-jet printing is that only limited materials have been ink-jet printed since it is difficult to prepare highly dispersed materials with small particle sizes that are able to produce fluid jets. In addition, only ultra-thin films (normally less than 1 µm, maximum of \(~10\ µm\)) have been printed, which restricts the areal capacitance of fMSCs. Micro-extrusion printing is promising in overcoming this problem.

1.4.3.4 Extrusion printing

Micro-extrusion printing is considered to be a more scalable patterning technique than ink-jet printing to obtain both 2D and 3D architectures (Figure 16d).\textsuperscript{[150,158,159]} This technique involves extrusion of a viscous ink through a nozzle mounted on a positioning stage with controlled speed and programmable trajectory. Sun et al. fabricated graphene-based interdigitated microelectrodes by extrusion printing of a concentrated GO aqueous solution (20 mg mL\(^{-1}\)).\textsuperscript{[150]} By tuning the needle diameter, extrusion rate and stage transcation velocity, they were able to print identical microelectrode structure with a line
width of ~600 µm and interline spacing of ~500 µm on a flexible PET substrate. After chemically reducing GO into rGO and coating with a layer of PVA-H$_2$SO$_4$, an all-solid-state fMSC with a high areal capacitance of ~19.8 mF cm$^{-2}$ and a volumetric capacitance of ~41.8 F cm$^{-3}$ was achieved. Despite limited use of extrusion printing in fabricating fMSCs, it has been widely applied in various other fields such as micro-batteries, biosensors, and solar cells. For example, 3D interdigitated microbattery (3D-IMA) architectures have been fabricated by printing concentrated lithium oxide-based inks.$^{[160]}$ The 16-layer 3D-IMA possesses an electrode with a width of ~60 µm and spacing of ~50 µm, indicating the great potential of extrusion printing technique in fabrication of higher resolution fMSCs with tailored 3D architectures.

In general, despite digital printing techniques such as ink-jet printing and extrusion printing having more specific requirements on ink properties including the particle size, concentration, viscosity, and rheology behaviour, they are both superior to screen printing and gravure printing in terms of the following merits: 1) both offer easy control over electrode layer thickness via layer-by-layer printing, which is a practical way to enhance the areal capacitance; 2) both allow the freedom of writing desired pattern parameters like the width and length of micro-electrodes, as well as the series/parallel connections between single devices; 3) also, and importantly asymmetric micro-electrodes (different materials for the positive and negative materials) can be individually printed. This impractical to achieve via other techniques; 4) since printable gel electrolyte has been developed recently and some packaging materials (like PDMS) are printable, this approach enables the realisation of a fully printed fMSC device. In addition, the digital printing of other micro-electronics is becoming a promising field, it provides the co-fabrication or integration of micro-SCs and external electronics in more complex circuit
architecture. Therefore, ink-jet printing and extrusion printing are the most promising
techniques in the fabrication of interdigitated microelectrodes and further efforts should
be paid in producing compatible inks.

1.5 Performance evaluation of flexible SCs

SCs act as a bridge between the energy source and energy outlet and are often combined
with other energy units for practical applications. However, the lack of a standardized
criterion to evaluate the performance of SC devices makes it difficult for developers and
manufactures to design and choose applicable fSC devices for integration into a specific
wearable electronic circuit or device.

Energy and power densities are two key parameters to evaluate the performance of a SC
device. The maximum energy $E$ (J) stored in a capacitor is proportional to the capacitance
$C$ (F) and the maximum operation voltage window $V$ (V) according to Equation 1.2:\[1^{[14]}\].
The maximum power ($P_{\text{max}}$) supplied by the SC device, i.e., the rate of energy delivery
per unit time, can be calculated by Equation 1.3, where $R_S$ is the equivalent series
resistance of the device\[14\]. Hence, excellent performance of a SC device can be achieved
not only by increasing the device capacitance, but also by widening the working voltage
range and minimizing the $R_S$\[16\].

\[E = \frac{1}{2} CV^2 \quad \text{Equation 1.2}\]
Many all-solid-state flexible SCs with excellent energy and/or power properties have been reported by researchers as the current state of the art. It is gradually being accepted that the traditional method of normalizing the device properties (e.g. capacitance, energy, power) by the mass of active materials is unreliable. This is because the mass of active materials is negligible compared with that of the device. In the past five years, an increasing number of reports evaluated the device performance in terms of the volume of the whole device. This approach can better reflect the realistic performance of the SC device in practical applications, especially when miniaturized wearable electronic systems allow limited space for their energy storage element. However, some of these devices are based on ultrathin electrodes with densely packed structure, which cannot be scaled up when electrode thickness increases due to the consequently increased electrode resistance and affected ion accessible surface area \[162-165\]. The high volumetric performance of these electrodes cannot be translated to high device performance when certain thicknesses of the electrode are required. Hence, to have a meaningful evaluation of the device performance, the properties of the fSC devices should be normalized to both the foot-print area and total volume of the device; including the electrodes, solid-state electrolyte, the separator, and current collectors. Furthermore, the thickness of the device and each component should also be provided for comparison.

Another key parameter to evaluate the performance of the fSC device is the flexibility and the mechanical properties of the device, which are necessary for the wearable energy storage devices to perform under various types of deformations such as stretching and

\[
P_{\text{max}} = \frac{V^2}{4R_s}
\]

Equation 1.3
bending. At present there is a lack of standardized methods to evaluate the mechanical properties of the electrodes, electrolyte or even the entire device. However, researchers have tried various ways to evaluate the mechanical properties of the fSC device and its components. For instance, the mechanical performance of the electrode film has been evaluated by repeatedly kinking, bending, and winding it, by crumpling it into a ball and by folding it into a paper crane and it was found that the electrode film did not fail under these series of destructive attempts.\textsuperscript{[166,167]} The electrode film has also been agitated, ultrasonicated and bent in water and ethanol and maintained its integrity indicating the robustness of the electrode film.\textsuperscript{[166,167]} Tensile testing is also an effective approach to evaluate the mechanical properties of the fSC electrode or device under stretching conditions.\textsuperscript{[166,167]} The investigation of the integrity and the capacitance performance of the fSC device under bending or twisting conditions has become a common method to evaluate the mechanical properties of the device.\textsuperscript{[142]} No changes in the electrochemical performance of the fSC device between flat, different bending angles, and various twisting conditions are indicative of a functional flexible device\textsuperscript{[142]}. In addition, fSCs will need to be robust enough to provide reliable operation under mechanical impact. Li \textit{et al.} also evaluated the electrochemical performance of the fSC device when the device was subjected to repeated impact forces (\textit{i.e.}, applying a swinging hammer with energy of \(\sim 2\) J).\textsuperscript{[156]} The slight changes in the electrochemical performance of the device under bending and impact tests indicate the suitability of the device for flexible and portable energy storage applications.
1.6 Thesis Objective

As outlined through this comprehensive literature review, research in all-solid-state flexible SCs over the last five years have made great progress in developing flexible electrode materials, seeking stable and efficient gel polymer electrolytes, investigating different device architectures and employing various electrode fabrication techniques. Nevertheless, it is still a significant challenge to develop flexible electrodes (both film electrodes and interdigitated electrodes) with high-performance and commercial level mass loading at large scale and in a cost-effective manner. Free-standing film electrodes are more promising than substrate-supported electrodes, as they enable the full utilization of the entire electrode and should be able to achieve higher energy density. However, the difficulty in pursuing thick film with high flexibility, stability and high performance is an obstacle. Laser-etching and extrusion printing are two simple and scalable techniques in fabricating interdigitated electrodes, while the lack of technically compatible electrode materials (i.e., large and flexible film electrode and printable electrode materials, respectively) greatly limits their application.

This thesis, therefore, aims to develop high performance electrodes for flexible SCs in simple and practically scalable ways. We expect to Electrode materials with high electrical conductivity and ion-accessible surface areas, which possess the potential to be fabricated into both free-standing flexible films and interdigitated electrodes will be prepared. The performance of fabricated SCs can be further optimized via tuning materials component ratio, film thickness, and device architectures.
In Chapter 3, free-standing, large-size and flexible reduced graphene oxide (rGO)-poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) films were prepared via a simple bar-coating method and assembled to be flexible all-solid-state SCs. Commercial PEDOT/PSS was selected as the flexible and conductive matrix, and at the same time, to prevent re-stacking of rGO layers. The component ratio of PEDOT/PSS and rGO was evaluated to achieve optimized film electrical conductivity and device performance. Meanwhile, the device performance as a function of electrode thickness was also investigated to pursue high areal capacitance.

Chapter 4 describes the facile generation of interdigitated patterned electrodes on large rGO-PEDOT/PSS films using the laser-etching technique. The novel fMSCs made with interdigitated patterned electrodes display superior performance in comparison to the fMSCs made from the conventional design outlined in Chapter 3. The simplicity and scalability of this process was demonstrated by generating ten interdigitated electrode patterns within 100 s. Electrode patterns, dimensions, and interconnects were easily adjusted by simply varying the laser etching parameters to achieve the optimized device performance (i.e., energy, power, current, and voltage).

The capacitance of the fabricated SCs in above chapters is mainly based on EDLC-type rGO, which is expected to be greatly increased via incorporating pseudo-capacitive materials. Meanwhile, via utilizing asymmetric design (i.e., EDLC-type material in negative electrodes, and pseudo-capacitive material in positive electrode), the energy density could be significantly improved by the expanded voltage window. To achieve this goal, another technique of extrusion printing was used to generate interdigitated electrodes, and technically compatible inks were therefore developed.
In Chapter 5, a new composite material was made by growing vertically aligned pseudo-capacitive polyaniline (PANi) nano-rods on both sides of the graphene oxide (GO) surface. The conductive PEDOT/PSS functioned as the stabilizer for the GO/PANi composite sheets. By tuning the synthesis conditions and formulation composition, we achieved aqueous-based GO/PANi-PEDOT/PSS (GO/PA-PE) inks with suitable rheological properties for extrusion printing. Printable rGO-PEDOT/PSS inks were also prepared via concentrating the dispersion used in Chapter 4 via rotary evaporation. The performance of extrusion printed GO/PA-PE symmetric fMSCs was optimized via tuning the component ratio and printed layers. In addition, an asymmetric design of a fMSC comprising of GO/PA-PE as the positive electrode and rGO-PEDOT/PSS as the negative electrodes was developed, which achieved improvements in operating voltage window, both energy and power densities, and cycling stability.

1.7 Reference


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ACS Nano 2015, 9, 5868.


Chapter 2  Experiment
2.1 Chemicals and reagents used

The chemical reagents and materials used in this work are listed in Table 2.1

Table 2.1 List of chemical reagents and materials used in this work.

<table>
<thead>
<tr>
<th>Reagent Name</th>
<th>Grade</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate)</td>
<td></td>
<td>Ajax Finechem</td>
</tr>
<tr>
<td>Graphite flakes</td>
<td>AR</td>
<td>Sigma-Aldrich</td>
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<tr>
<td>Concentrated sulfuric acid (98% H₂SO₄)</td>
<td>AR</td>
<td>Chem-Supply</td>
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<tr>
<td>Ortho Phosphoric Acid (85% w/w H₃PO₄)</td>
<td>AR</td>
<td>Chem-Supply</td>
</tr>
<tr>
<td>Hydrochloric Acid (32% HCl)</td>
<td>AR</td>
<td>RCI Labscan</td>
</tr>
<tr>
<td>Hydrogen Peroxide (30% H₂O₂)</td>
<td>AR</td>
<td>Chem-Supply</td>
</tr>
<tr>
<td>Potassium Permanganate (KMnO₄)</td>
<td>AR</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
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<td>AR</td>
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</tr>
<tr>
<td>Aniline</td>
<td>AR</td>
<td>Sigma-Aldrich</td>
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<tr>
<td>Ammonium Persulfate (APS)</td>
<td>AR</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Diethylene Glycol</td>
<td>AR</td>
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<td>Hypophosphorous acid solution (50 wt.% H₃PO₂ in H₂O)</td>
<td>AR</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Chloroform</td>
<td>AR</td>
<td>Honeywell Burdic &amp; Jackson</td>
</tr>
</tbody>
</table>
2.2 Sample preparation and characterization techniques.

2.2.1 Sample preparation related techniques

2.2.1.1 Metal sputter coater

Sputter coating was performed using an EDWARDS FTM6 Auto 306 (Figure 2.1). A thin layer (100 ~200 nm) of Au was sputter coated onto the substrates or electrode films, which would act as current collector in a supercapacitor device. It improves the current collecting capabilities of electrode materials, charge storage and delivery, while minimizing the equivalent resistance (ESR) loss. Shown in Figure 2.1b and c are photos of PET film before and after Au sputter coating.

Figure 2.1 (a) Photograph of Edwards FTM6 Auto 360 Sputter coater, (b) a PET film stuck on an acrylic sheet, and (c) Au sputter coated PET film.
2.2.1.2 *Ultra-sonication*

Ultra-sonication was used to help materials disperse uniformly in the solvent (*e.g.* water). The sonication techniques used in this work were bath sonication and probe sonication respectively. A Branson B5500R-DTH bath sonicator (Figure 2.2a) was used to disperse mixed composite materials (*e.g.* Graphene oxide and PEDOT/PSS in water). The probe sonicator (Branson Digital Sonifier Model 102C) (Figure 2.2b) is a stronger sonication technique, which can not only speed dissolution, but also break intermolecular interactions and break graphene sheets. As shown in Figure 2.2c, an acidic treated carbon nanotube can be dispersed in water after probe sonication. It was used in a pulsed method (2 seconds on, 1 second off) at 450 W, 20 Hz. Varying sonication times and amplitude were used for different materials.

![Photographs of (a) Branson B5500R-DTH bath sonicator, (b) Branson Digital Sonifier Model 102 C, and (c) probe sonicated acidic treated carbon nanotube dispersion.](image)

Figure 2.2 Photographs of (a) Branson B5500R-DTH bath sonicator, (b) Branson Digital Sonifier Model 102 C, and (c) probe sonicated acidic treated carbon nanotube dispersion.
2.2.1.3 Centrifugation

Centrifugation of graphene oxides and their composites dispersed in various solvents for purification purpose was performed using an Eppendorf centrifuge 5702 (Figure 2.3).

![Figure 2.3 Photograph of Eppendorf centrifuge.](image)

2.2.1.4 O₂ plasma treatment

Oxygen plasma refers to plasma treatment performed while introducing oxygen to the plasma chamber[1]. It was used in this work to increase the wettability of a substrate (e.g. PET film, PDMS), after which the ink materials can be extrusion printed well on the substrate. It was performed using a Harrick Plasma Cleaner PDC-32G-2 and Plasmaflo PDC-FMG (Figure 2.4) with air flow kept at 1100 mTorr and exposure time of 1 min. As shown in Figure 2.4b and c, the contact angle between a graphene oxide (GO)/polyaniline(PANI)-PEDOT/PSS aqueous ink decreased from 110.9 ° to 46.6 ° after plasma treatment on the PDMS substrate, indicating that the oxygen plasma greatly increased the wettability of PDMS.
Figure 2.4 (a) Photograph of Plasma Cleaner PDC-32G-2 and Plasmaflo PDC-FMG, and contact angles between aqueous ink and PDMS substrate (b) before and (c) after plasma treatment on PDMS substrate.

2.2.2 Physical characterization techniques

2.2.2.1 Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) is used to capture the surface and cross-sectional morphologies of film samples in this work. SEM obtains the information of sample’s surface topography by scanning the sample with a focused beam of electrons. It generally scans in a raster scan pattern and produces an image by combining the beam’s position with the detected signal.\(^2\)

A JEOL JSM-7500FA field emission SEM (Figure 2.5a) was used in this work in which the accelerating voltage was set at 5.0 kV, emission current was 10 mA and the working distance was 8 mm. Samples were mounted to the sample holder using double-sided conductive carbon tape for observation. For preparing cross-sectional sample, the film
samples were immersed into liquid nitrogen and then broken using two tweezers. Shown in Figure 2.5b is a typical SEM image of graphene oxide/polyaniline (GO/PANi) with high resolution, where the PANi nanorod vertically aligned on both side of graphene oxide sheets.

Figure 2.5 (a) Photograph of JEOL-7500FA field emission gun scanning electron microscope (SEM) and (b) SEM image of GO/PANi sample.

2.2.2.2 Optical microscopy (Leica DM6000)

The optical microscope uses visible light and a system of lenses to magnify images of small samples. It was used to observe the dimensions of laser-cut and extrusion printed interdigitated microelectrode patterns in this work. The optical microscope system used in this work is Leica DM6000 (Figure 2.6a) the images were captured using a CCD camera and recorded by a computer. The optical microscope image of an extrusion printed antenna is shown in Figure 2.6b, from which a line width of ~300 µm is observed.
Figure 2.6 (a) Photo of Optical Microscopy, Leica DM6000 and (b) Optical microscope image of extrusion printed antenna.

2.2.2.3 *Thermo-gravimetric analysis (TGA)*

Figure 2.7 (a) Photo of the TGA Q500 system and (b) TGA curve of the reduced graphene oxide (rGO) sample.
Thermo-gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).[3] In this study, TGA was carried out in air using Q500 (TA Instruments) (Figure 2.7) with data analysis carried out using the Q Series software V. 2.5.0.255. The temperature range studied is between 50 °C to 1000 °C at a rate of 5 °C min⁻¹. Figure 2.7b shows the TGA curve of reduced graphene oxide (rGO) sample. It can be seen that the steepest weight loss was shown at 600 °C, and all the rGO was burnt out at 700 °C.

2.2.2.4 X-ray diffraction (XRD)

X-ray Diffraction (XRD) is a non-destructive analytical technique that could be used to reveal the structural information, such as chemical composition, crystal structure, crystallite size, strain, preferred orientation and layer thickness.[4] In this study, we use XRD to identify the interlayer spacing of graphene in reduced graphene oxide, graphene oxide, and graphene-based composites.

The crystal structure of a material can be regarded as being built of layers, or planes, which each act as a semi-transparent mirror. X-rays with a wavelength similar to the distances between these planes can be reflected such that the angle of reflection is equal to the angle of incidence. We call this behavior ‘diffraction’ and it is described by Bragg’s Law (Equation 2.1), in which \( \lambda \) is the wavelength of incident wave, \( \theta \) is angle, \( n \) is the order of the reflection, \( d \) is the interlayer space between layers.[5] The XRD used in this work was performed on a GBC MMA XRD (\( \lambda = 1.54 \, \text{Å} \)) with the voltage and current kept at -40 kV and 25 mA respectively (Figure 2.8a).[6] For graphene-based materials, the order
of reflection (n) is 1, the interlayer distance (d) can be calculated when the diffraction angle was detected. A typical XRD pattern of GO is shown in Figure 2.8b, in which a typical peak of the (002) diffraction at 2θ=8.8° was observed and a interlayer-spacing (d) of 0.94 nm was calculated according to the Bragg’s Law.

\[ 2d \sin \theta = n\lambda \]

Equation 2.1

Figure 2.8 (a) Photograph of GBC MMA XRD machine used for XRD experiments and (b) a XRD pattern of GO.

2.2.2.5 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a sample. The absorption peaks represent a molecular ‘fingerprint’ of the sample and can be used to identify different chemical structures (molecules), which are particularly for identification of organic and polymer materials.[7] In this study, it was carried out using the Shimadzu FTIR Prestige-21 (Shimadzu Scientific Instruments, Australia) (Figure 2.9a) to analyse the chemical
bonding of graphene, PEDOT/PSS and PANi samples and their composites. Figure 2.9b displayed the FT-IR spectrum of the polymer of PEDOT/PSS. It can be seen the signal of functional groups in polymers can be detected.

Figure 2.9 (a) Photograph of the Shimadzu FTIR Prestige-21 and (b) FT-IR spectrum of PEDOT/PSS.

2.2.2.6 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique that provides information about molecular vibrations and can be used for sample identification and quantitation. In this work, Raman spectra were used to determine the surface functionality of graphene oxide and reduced graphene oxide, and identify the existence of conducting polymers (like PEDOT/PSS and PANi). It was carried out ON A Jobin-Yvon Horiba 800 using a 632.81 nm laser (Figure 2.10a). The data analysis was carried out using Labspec V.5.45.09 software. Shown in Figure 2.10b is the Raman spectrum of PEDOT/PSS and the signature peaks for this sample were found.
1.1.1.1 Rheometry (Specified to Chapter 5)

Viscosity is an important parameter to the printability of inks. Generally, the required viscosity ranges are \( \sim 10^{-3} \) Pa\( \cdot \)s and \( 10^{3} \sim 10^{4} \) Pa\( \cdot \)s at 1 s\(^{-1}\) for inkjet printing and traditional extrusion-based 3D printing, respectively. Inks with values between these two ranges could be used in extrusion printer. Meanwhile, shear thinning behavior of inks are also required in extrusion printing. In this work, an AR G2 Rheometer (TA Instrument Ltd) (Figure 2.11a) with a cone-and-plate system was employed to measure the viscosity (\( \eta \)) of inks for extrusion printing. Cone angle was 2 degrees and 36 seconds, cone diameter 40 mm and cone truncation 55\( \mu \)m. Sample volume used was 1 mL for all measurements and the shear rate range was set from 0.1 s\(^{-1}\) to 1000 s\(^{-1}\). The viscosity measurement of PEDOT/PSS aqueous dispersion (25 mg mL\(^{-1}\)) in Figure 2.11b shows that the dispersion has a high viscosity of 3.9 Pa\( \cdot \)s at a low shear rate of 1 s\(^{-1}\), and exhibit typical shear thinning behavior.

Figure 2.10 (a) Phptograph of Raman spectroscopy apparatus, Jobin-Yvon Horbia 800 and (b) Raman spectrum of PEDOT/PSS.
Contact angle measurements (Specified to Chapter 5)

Contact angle measurement is a simple, rapid and sensitive method to measure the surface wettability of the substrates. The lower the contact angle, the more ink can spread better on the substrate to form uniform film. By contrast, on substrates with high contact angle (\(>90^\circ\)), the inks gathered to form uncontacted spots. In this work, contact angle measurements were performed using a Contact Angle System OCA Data physics gonimeter (Figure 2.12) with software SCA202 V.3.11.6. During the measurement, 5\(\mu\)L ink droplet was dispensed from a standard syringe and placed onto the substrate surface. After photographing the water droplet, the contact angles were measured using the software. A minimum of 3 measurements were taken for each sample, and then an average value was calculated and reported. Shown in Figure 2.12b is a contact angle measurement between an aqueous based ink and glass slide.
Figure 2.12 (a) Photograph of Gonimeter used for contact angle measurement and (b) an example of contact angle test.

2.2.2.8 Profilometry

Profilometer is a measuring instrument to measure a surface’s profile and quantify its roughness. In profilometer, a diamond stylus moves vertically in contact with a sample and then moved laterally across the sample for a specified distance and contact force. The height and lateral position of the diamond stylus generates an analog signal which can be converted into a digital signal, stored, analyzed, and displayed. In this work, a Dektak 150 stylus profilometer (Figure 2.13) was used to measure the thickness of as-prepared electrode films and printed microelectrodes. During the stylus measurement, the stylus force adopted was 3 mg with a 10 mm scan range and 0.1 µm/sample resolution. Roughness of samples can also be obtained from this measurement. Shown in Figure 2.13b and c is the illustration of thickness measurements and thickness profiles of the printed microelectrodes.
2.2.2.9 Conductivity (four-probe conductivity)

Conductivity measurements on prepared films were performed on a Jandel Model RM3 four probe system. The system uses separate pairs of current-carrying or voltage-sensing electrodes to make more accurate measurements than the simple and more usual two-terminal sensing. It can eliminate the lead and contact resistance from the measurement. As shown in (Figure 2.14), the system calculated the resistance from the measured voltage value between the connections 2 and 3, while the current is supplied via for connections of 1 and 4. The conductivity of films $\sigma$ (S cm$^{-1}$ or S m$^{-1}$) can be calculated from the sheet resistance $R$ (\(\Omega/\square\)) by Equation 2.2, where $T$ (cm or m) is the thickness of the sample.\cite{10}
\[ \sigma = \frac{1}{R \times T} \]  

Equation 2.2

Figure 2.14 Photograph of a Jandel Model RM3 four probe system

2.3 Device fabrication and electrochemical characterization

2.3.1 Device fabrication

2.3.1.1 Sandwiched structured supercapacitor (SSCs)

2.3.1.1.1 Bar-coating of electrode film.

Free-standing and flexible electrode film was prepared via a bar-coating method. The as-prepared aqueous dispersion of electrode materials was sonicated (Branson B5500R-DTH bath sonicator, low power) for 30 minutes prior to use. The mixture was bar-coated on a substrate (e.g., PVDF membrane, PET, glass, etc.) with glass slides (use side face) encircled to fix films’ shape and size. The thickness of the film was controlled by the
volume of dispersion used per unit area of the film. The film was first dried overnight at room temperature and then heated in a 60 °C oven (air atmosphere) overnight to evaporate the remaining water and DEG. The flexible electrode film was then peeled off from the substrate if needed.

2.3.1.1.2 Device assembly.

Figure 2.15 Schematic illustration of the sandwiched structured flexible supercapacitors.

Free-standing film electrodes were assembled into two electrode all-solid-state symmetric supercapacitor devices by the following methods as shown in Figure 2.15. A H₃PO₄/PVA gel electrolyte was prepared by mixing PVA powder (4 g), H₃PO₄ (6 g) and deionized water (40 mL) together. The mixture was heated to around 85 °C under magnetic stirring until the solution became clear. 150 nm gold was sputter coated directly on one side of electrode film which served as current collector. Hot PVA/H₃PO₄ electrolyte (heated to 85 °C prior to use) was drop cast onto the other side of the electrode films. Films were left in air overnight to evaporate most of the water contained in electrolyte. Two films
were then pressed together (with both of the electrolyte side pressed face-to-face) to form an all-solid-state flexible symmetric supercapacitors.

2.3.1.2 Laser-etched microsupercapacitors (MSCs) (Specified to Chapter 4)

The second part of this work (Chapter 4) involved utilizing a laser cutter (Figure 2.16a) to prepare interdigitated microelectrodes for fMSCs and the schematic illustration of fabricating laser-etched fMSCs is shown in Figure 2.16b. The interdigitated finger electrodes were patterned on the prepared films (bar-coated electrode film on Au coated PET) by a 10.6 µm CO₂ laser cutting system (Universal PLS6MW Multi-Wavelength Laser Platform, 30 W, spot size of ≈25 µm, Figure 2.16a) under ambient conditions. First, layers of active materials and Au were selectively etched to form interdigitated patterns. The laser power was set between 5% and 25% depending on film composition and thickness and the scan speed fixed at 10%. Interdigitated electrodes were patterned with a length (L) of 8 mm, an interspacing distance (d) of 100 µm between two neighboring finger electrodes, and with different widths (W) ranging from 212 µm to 2.4 mm depending on the number of fingers in a total area of 1 cm × 1 cm. Then two square-shaped electrical contact pads (3 mm × 3 mm) connecting positive and negative electrodes were formed by etching only the active materials layer leaving the Au layer.

Patterned electrodes were assembled into all-solid-state fMSCs by the following methods. First, sliver paint (Ted Pella) was applied on the contact pads, followed by extending with conductive copper tapes, which were connected to electrochemical workstation during testing. A hot polymer gel electrolyte PVA-H₃PO₄ (heated to 85 °C prior to use) was then drop cast onto the projected area and solidified in air overnight.
2.3.1.3 Extrusion printed MSCs (Specified to Chapter 5)

Symmetric fMSCs were produced by directly extrusion printing active materials on Au pre-patterned PET film. The schematic illustration of fabricating laser-etched fMSCs is shown in Figure 2.17b. A thin layer of Au (200 nm) was sputter coated on a flexible PET film through the custom-made interdigital finger mask with two square-shaped contact pads connected to the positive and negative electrodes. The as-prepared inks were then carefully printed on the pre-patterned Au using an extrusion printer (KIMM SPS1000, Figure 2.17a) with X-Y-Z motion control system and positioning resolution of 1 µm. A dispensing tip (100 µm in inner nozzle diameter) was used to print the inks at an applied gas pressure ranging from 5 to 30 kPa (pressure varied for different dispersion to keep the flow rate at ~5 µL min⁻¹). The tip moving speed was set at 400 mm min⁻¹ and the tip-to-substrate distance was varied from 50 µm to 100 µm. To facilitate the solvent evaporation, the substrate was heated to 40 °C during the printing process. After printing, the printed electrodes were dried in an oven at 60 °C overnight (in air) to remove all
solvents. In order to assemble the extrusion printed patterned electrodes into all-solid-state fMSCs, the two contact pads were first extended with conductive copper tapes to provide good connections to electrochemical workstation during testing. A PVA-H$_3$PO$_4$ gel electrolyte was separately prepared according to the previously reported method$^{[11]}$ and heated to 85 °C prior to use. The hot polymer gel electrolyte was then cast onto the interdigitated electrodes while the rest of the electrodes had been covered by Kapton polyimide tape to prevent contact with the electrolyte. The all-solid-state fMSCs were ready to test after air-drying the electrode overnight.

Figure 2.17 (a) Extrusion Printing system (KIMM SPS1000 extrusion printer) and (b) schematic diagram of the fabrication of extrusion printed fMSC.

The asymmetric fMSCs with GO/PANi-PEDOT:PSS as the positive electrode and rGO-PEDOT:PSS as the negative electrode was assembled in the similar method. The only difference was the extrusion printing process where the positive and negative inks were stored in separated syringes and printed on the pre-patterned Au current collectors.
2.3.2 Electrochemical analysis techniques

Electrochemical performances of as-prepared electrode materials and fabricated supercapacitor devices were investigated by the following techniques including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Galvanostatic charge/discharge (GCD) in either a three-electrode or two electrode set-up.

2.3.2.1 Cyclic voltammetry (CV)

Cyclic voltammetry is a widely used technique in electrochemistry at laboratory scale, as it is an accurate technique that enables qualitative and pseudo-quantitative studies, kinetic analysis by scanning a huge range of scan rates and voltage window determination. It applies a linear voltage ramp to an electrode (or a device) between two voltage limits and measures the resulting current.\[^{[12]}\]

In this work, the CV was performed using a CHI720 electrochemical work station, and the applied scan rates varied from 1 mV s\(^{-1}\) to 5000 mV s\(^{-1}\). Evaluations like specific capacitance, energy and power density were calculated from the CV curve at per scan rate.

In three electrode system, the capacitance (C, F) is calculated according to Equation 2.3, where \(\int IdV\) is the integrated area of the CV curve, \(U\) is the voltage window (V), \(S\) is the scan rate (V s\(^{-1}\)). Specific capacitance of the working electrode is calculated via dividing the capacitance by the mass of electrode materials.
\[ C = \frac{\int I \, dV}{2 \times U \times S} \quad \text{Equation 2.3} \]

\[ C_{sp} = \frac{C}{M} \quad \text{Equation 2.4} \]

In two electrode systems, capacitance of the device (\( C_D \)) is calculated as Equation 2.5 once again, while the capacitance per electrode (\( C_E \)) is 2 times of the device capacitance (Equation 2.6). Once again \( \int I \, dV \) is the integrated area of the CV curve, \( S \) is the scan rate \( U \) is the voltage window (V), \( S \) is the scan rate (V s\(^{-1}\)). Specific capacitance of either per electrode (\( C_{Esp} \)) or device (\( C_{Dsp} \)) based on mass (\( M_D \) or \( M_E \), g), area (\( A_D \) or \( A_E \), cm\(^2\)) or volume (\( V_D \) or \( V_E \), cm\(^3\)) was calculated according to Equation 2.7 or Equation 2.8. The unit of calculated specific capacitance based on mass, area or volume is F g\(^{-1}\), F cm\(^{-2}\) or F cm\(^{-3}\), respectively.

\[ C_D = \frac{\int I \, dV}{2 \times U \times S} \quad \text{Equation 2.5} \]

\[ C_E = 2 \times C_D \quad \text{Equation 2.6} \]

\[ C_{Dsp} = \frac{C_D}{M_D \text{ or } A_D \text{ or } V_D} \quad \text{Equation 2.7} \]

\[ C_{Esp} = \frac{C_E}{M_E \text{ or } A_E \text{ or } V_E} \quad \text{Equation 2.8} \]

The energy density (\( E \)) and power density (\( P \)) of the supercapacitor devices were calculated as Equation 2.9 and Equation 2.10. Units are W h g\(^{-1}\), Wh cm\(^{-2}\) or Wh cm\(^{-3}\) for
energy density, and \( W \, g^{-1} \), \( W \, cm^{-2} \) or \( W \, cm^{-3} \) for power density based on various standards (i.e., mass, area or volume respectively).

\[
E = \frac{1}{2 \times 3600} QU = \frac{1}{2 \times 3600} C_{Dsp} U^2 = \frac{1}{8 \times 3600} C_{Esp} U^2 \quad \text{Equation 2.9}
\]

\[
P = \frac{3600 \times E}{\Delta T_d} = \frac{3600 \times E}{U/S} \quad \text{Equation 2.10}
\]

2.3.2.2 Galvanostatic charge/discharge (GCD)

Galvanostatic charge/discharge, is a technique very different from cyclic voltammetry, where the constant current is controlled and the voltage is measured. In this work, it was carried out with a Neware Galvanostat (100 mA, 5 V, Figure 2.18a) equipped with Test Control V.5.0 software on two-electrode set up (i.e., supercapacitor device). The potential window studied was between 0 V to 0.8 V, 0 V to 1.0 V, or 0 V to 1.2 V depending on the quality of electrode materials and device design. Figure 2.18b is a typical charge/discharge curves of a rGO-PEDOT/PSS supercapacitors carried at a current density of 0.1 A g\(^{-1}\). Calculations for device capacitance \( C_D \) can be obtained by Equation 2.11, where the \( I_d \) is constant current used for charging and discharging (A), and \( \Delta T_d \) is the discharge time (s). Other evaluations (e.g., \( C_E \), \( C_{Dsp} \), \( C_{Esp} \)) were calculated according to Equation 2.4~2.6.

\[
C_D = \frac{I_d \times \Delta T_d}{U} \quad \text{Equation 2.11}
\]
2.3.2.3 **Electrochemical impedance spectroscopy (EIS).**

Electrochemical impedance spectroscopy is used to measure the impedance of a system by applying a small AC potential over a range of frequencies. It reveals the
electrochemical process in an electrode system such as electron transfer and time constant.

In this study, the EIS is performed using Solartron SI1260 Impedance Analyzer and EG&G Instruments Princeton Applied Research Potentiostat/Galvanostat Model 283 (Figure 2.19) employing a frequency range of 100 kHz to 0.01 Hz and an AC amplitude of 10 mV at open circuit potential. Figure 2.19b shows a typical EIS spectrum of a PEDOT/PSS supercapacitor device.

2.4 Reference

Chapter 3 High-Performance Flexible All-Solid-State Supercapacitor from Large Free-Standing Graphene-PEDOT/PSS Films

This chapter is adapted from the article, “High-Performance Flexible All-Solid-State Supercapacitor from Large Free-Standing Graphene-PEDOT/PSS Films”, by Yuqing Liu, Bo Weng, Joselito M. Razal, Qun Xu, Chen Zhao, Yuyang Hou, Shayan Seyedin, Rouhollah Jalili, Gordon G. Wallace, and Jun Chen” that was published in Scientific Reports (2015, 5, 17045). Adapted with permission from Nature Publishing Group.
3.1 Introduction

The development of flexible electrodes, which exhibit high capacitance and high electrical conductivity to ensure fast charge-discharge, is one of the most crucial factors for fabricating flexible SCs.

A common method to make flexible electrode is by depositing electroactive materials on soft and flexible substrates with porous structure. For example, carbon dispersions (carbon nanotubes, graphene oxide etc.) have been deposited as inks on cellulose papers\(^1\), porous cotton\(^2\) and synthetic polymer sponges\(^3\). Conducting polymers, such as polypyrrole\(^4\), polyaniline\(^5\) or poly(3,4-ethylenedioxythiophene)(PEDOT)\(^6\) have been directly deposited on soft and porous substrates via chemical or electrochemical polymerization. Despite their high flexibility and good ion accessibility, the electrical conductivity of these electrodes has been limited by insulating properties of substrates used affecting the charge-discharge rate of SCs. In addition, the total SC device weight increased due to the use of insulating substrates, leading to a decrease of capacitance per unit weight.

To resolve this problem, some researchers have prepared free-standing flexible electrodes using vacuum filtration\(^7\)–\(^9\) or spray coating active materials on flexible PET film\(^10\)–\(^12\) to create super-thin electrode films. SC devices made from these electrodes often exhibit high gravimetric capacitance. However, the gravimetric capacitance is not maintained when the mass loading or thickness of the films is increased, making them unsuitable for practical applications. The capacitance further decreases when solid-state electrolyte is used because large electrolyte ions could not penetrate into the densely packed electrode...
materials\textsuperscript{[9]}. In addition, the device flexibility suffers when thicker electrodes are used. Fabrication of highly flexible SC electrode materials with outstanding performance remains a challenge.

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) is considered a promising material for SC electrodes. Compared with other conducting polymers (like PANi and PPy), it is superior in terms of electrical conductivity, chemical and electrochemical stability, and dispersibility in various solvents\textsuperscript{[13–15]}. Reduced graphene oxide (rGO) is another promising SC electrode material. It has a high capacitance and an extremely long cycle life due to the ultrahigh specific surface area and the electric double layer mechanism that is the basis of the charge-discharge process. However, the capacitance of pure rGO films is often limited by re-stacking of layers\textsuperscript{[16–20]}. Therefore, additives which can prevent re-stacking and simultaneously enhance electrochemical performance have been incorporated into rGOs when used as SC electrodes\textsuperscript{[16–20]}.

In this chapter, we successfully prepared free-standing, large-area and flexible rGO-PEDOT/PSS composite membranes \textit{via} a simple bar-coating method. We demonstrate that these membranes are highly flexible and can be rolled to fabricate SC devices. Commercial PEDOT/PSS was selected as the conductive matrix to prevent re-stacking of rGO layer and at the same time, to impart additional flexibility to the electrodes. The composite films demonstrated high flexibility and conductivity, and when assembled into all-solid-state SCs using PVA-H\textsubscript{3}PO\textsubscript{4} gel as electrolyte, the devices could be bent at any angle without a significant decrease in electrochemical performance. We demonstrate that the rolled-up SC devices can power a green LED light for 20 seconds when fully charged.
3.2 Experiment

3.2.1 Synthesis of graphene oxide

Graphene Oxide (GO) dispersion was prepared using the modified Hummers method\cite{21}. Firstly, a mixture of concentrated H$_2$SO$_4$/H$_3$PO$_4$ (360:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt. equiv.) and KMnO$_4$ (18.0 g, 6 wt. equiv.). The reaction was heated to 50 °C and stirred for 14.5 hrs, cooled to room temperature, and poured onto ice (~400 mL) with 30 % H$_2$O$_2$ (20 mL). The mixture was then stirred for 30 min and centrifuged at 4,400 rpm for 20 min. The precipitate was washed and centrifuged with HCl solution (9:1 water/HCl by volume) twice and then dispersed in water and dialyzed for 7 days. The graphene oxide dispersion was finally obtained by probe sonicating (Branson Digital sonifier, 400 watt, 38 % amplitude) the purified graphite oxide dispersion for 1 hr, with a pulse of two seconds on and one second off, totally 1.5 hrs.

3.2.2 Preparation of large PEDOT/PSS flexible film

PEDOT/PSS pellets were dispersed in deionized water at a concentration of 20 mg mL$^{-1}$ by magnetic stirring and then diethylene glycol (DEG) was added to the dispersion at 37.2 mg mL$^{-1}$. The dispersion was stirred overnight and then sonicated (Branson B5500R-DTH bath sonicator, low power) for 30 minutes prior to use. The mixture was bar-coated on a hydrophilic PVDF membrane as described in Chapter 2.3.1.1.1. A flexible PEDOT/PSS film was then peeled off from the PVDF membrane.
3.2.3 Preparation of rGO-PEDOT/PSS flexible films

The composite dispersions were prepared by the addition of PEDOT/PSS into the GO dispersions. Samples with various GO loadings of 20 wt. %, 33 wt. %, 50 wt. %, 67 wt. % and 80 wt. % were prepared. In each sample, the total concentration (solid content) of PEDOT/PSS and GO was kept at 20 mg mL\(^{-1}\). Diethylene glycol was added to each sample at 33.2 mg/mL\(^{-1}\). GO-PEDOT/PSS films were prepared the same way as PEDOT/PSS films. All films were immersed in 5 wt. % HPA and then heated to 60 \(^{\circ}\)C for 24 hours, rinsed with water and dried at room temperature.

3.2.4 Device Assembly

The flexible all-solid-state supercapacitor devices were assembled using the PEDOT/PSS, GO-PEDOT/PSS, rGO-PEDOT/PSS and rGO electrode films as described in Chapter 2.3.1.1.

3.3 Results and Discussions.

3.3.1 Flexible and conductive PEDOT/PSS film

3.3.1.1 Photo images and SEM images of flexible PEDOT/PSS film

A large-size (30 cm × 7 cm) free-standing PEDOT/PSS-DEG film was prepared by bar-coating a thin layer of PEDOT/PSS and diethylene glycol (DEG) solution as described in experimental section. The digital photographs of the free-standing PEDOT/PSS film (14 μm thickness) shown in Figure 3.1a and b illustrate that it is highly flexible and can be bent and twisted. Ethylene glycol and DEG are commonly used secondary dopants to
improve the conductivity of PEDOT/PSS\textsuperscript{[13,22-27]}\textsuperscript{.} A PEDOT/PSS film without DEG (pristine PEDOT/PSS) was also prepared under the same condition as a control. The PEDOT/PSS-DEG has a high electrical conductivity (230 S cm\textsuperscript{-1}), which is nearly two orders higher than pristine PEDOT/PSS (3.2 S cm\textsuperscript{-1}). This difference in conductivity can be explained to be the result of phase separation of the excess insulating PSS domains from the PEDOT/PSS domains induced by DEG to create a highly conducting PEDOT/PSS network\textsuperscript{[13]}.

Figure 3.1 (a) and (b) Photographs of the as-prepared large size (30 cm × 7 cm), free-standing, and highly flexible PEDOT/PSS film.

Figure 3.2 Cross-sectional SEM images of (a) pristine PEDOT/PSS film and (b) PEDOT/PSS with DEG film

A scanning electron microscopy (SEM) study of the cross-sections of the films reveal
more macro-scale porosity in PEDOT/PSS-DEG film (Figure 3.2b) compared to the pristine PEDOT/PSS film (Figure 3.2a). It is assumed that the micro sized pores were previously occupied by DEG when the films were dried at room temperature. Most of the DEG during this step was removed upon oven drying and created macro pores.

3.3.1.2 Electrochemical performance of PEDOT/PSS film

![Graphs showing electrochemical performance of PEDOT/PSS film](image)

Figure 3.3 (a) CVs (50 mV s\(^{-1}\)) and (b) Specific capacitance comparison between PEDOT/PSS electrodes with and without DEG. (c) CV curves of PEDOT/PSS-DEG supercapacitor device at different scan rates. (d) Electrochemical impedance spectrum (EIS) of PEDOT/PSS-DEG device.

To compare the electrochemical performance, PEDOT/PSS films with and without DEG
were assembled into supercapacitor devices. The PEDOT/PSS-DEG device exhibit superior performance to pristine PEDOT/PSS device in terms of CV area (Figure 3.3a) and calculated specific capacitance of electrode (Figure 3.3b), because the increase in porosity in the PEDOT/PSS-DEG film has increased the accessible surface area. Furthermore, the PEDOT/PSS-DEG film can retain a highly rectangular CV curve when the scan rate was increased to 200 mV s⁻¹ (Figure 3.3c), indicative of high charge mobility. The small semi-circle in the high frequency domain of the electrochemical impedance spectra (EIS) (Figure 3.3d) also showed low polarisation resistance, indicating fast diffusion of electrolyte ions. These results suggest that the treatment with DEG enhanced the electrical conductivity and porosity of the PEDOT/PSS film significantly as was reflected in the higher specific capacitance. This treatment method was therefore utilized in the preparation of rGO-PEDOT/PSS films and all the samples in the following statement without specific illustration were treated with DEG.

3.3.2 Physical characterization of rGO-PEDOT/PSS films.

3.3.2.1 Scanning Electron Microscopy (SEM)

Figure 3.4 shows the cross-sectional SEM images of rGO, PEDOT/PSS and rGO-PEDOT/PSS composite films. The pristine rGO film (Figure 3.4a) has a layered structure with closed edges, which is formed by re-stacking and interlocking of individual sheets. Such a densely stacked structure has previously been shown to hinder the electrolyte ion diffusion, resulting in an insufficient utilization of rGO’s potential capacitance⁸,¹⁶,¹⁷,²⁸. When PEDOT/PSS and DEG were incorporated into this system (i.e. forming the rGO-PEDOT/PSS film), the cross-section of the film displayed an open edge that could be seen under SEM (Figure 3.4c and e). This open edge indicates that the presence of
PEDOT/PSS and DEG have effectively prevented the re-stacking of individual graphene sheets and provided a higher accessible surface area. In addition, the hydrophilic property of PEDOT/PSS can also help electrolyte ions to penetrate into and access the inner surface of the electrode materials. Images of the composite film without DEG were shown in Figure 3.4d and f for comparison. It was found that there is still some re-stacking of several layers of rGO sheets that are separated by PEDOT/PSS. The space between two single layers appears smaller than samples with DEG although it is much larger than pure rGO, showing the addition of DEG in the composite films can also increase the porosity and surface area as in PEDOT/PSS film.
Figure 3.4 SEM cross-section images of the various films (a) rGO, (b) PEDOT/PSS, (c) rGO-PEDOT/PSS with DEG, (d) rGO-PEDOT/PSS without DEG, (e) rGO-PEDOT/PSS with DEG (higher magnification) and (f) rGO-PEDOT/PSS without DEG (higher magnification)
3.3.2.2 X-ray diffraction (XRD)

Both pristine and composite materials were also investigated using X-ray diffraction (XRD) measurements. The XRD patterns of PEDOT/PSS, GO, rGO, GO-PEDOT/PSS and rGO-PEDOT/PSS are shown in Figure 3.5. PEDOT/PSS exhibited a peak at $2\theta = 25.9^\circ$, which is related to the (020) plane of the PEDOT/PSS polymer backbone [29]. This peak is also observed in the XRD spectra of GO-PEDOT/PSS and rGO-PEDOT/PSS. For GO and GO-PEDOT/PSS, the distinct peaks were found at $2\theta = 8.8^\circ$ and $7.6^\circ$, respectively. These peaks are correlated to the (002) diffraction of GO sheet, from which the interlayer $d$ spacing values have been calculated to be 0.94 nm and 1.16 nm according to Bragg’s law (equation (1), where n=1, $\lambda$ is the wavelength of incident wave (1.54 Å)) [30], respectively. This slight increase of interlayer spacing in GO-PEDOT/PSS composite film

Figure 3.5 XRD patterns of the rGO, GO, PEDOT/PSS, GO-PEDOT/PSS, rGO-PEDOT/PSS, and rGO-PEDOT/PSS without DEG films
could be attributed to the good interaction of PEDOT/PSS with individual GO sheets and their intercalation in between GO layers\textsuperscript{[31]}. After reduction by hypophosphorous acid (HPA)\textsuperscript{[32]}, the specific GO peaks at around $10^\circ$ disappeared in both rGO and rGO-PEDOT/PSS samples and broad peaks were observed at around $2\theta = 24.1^\circ$ for rGO and $2\theta = 18.5^\circ$ for the composite film. These peaks corresponded to interlayer distance that decreased to 0.37 nm and 0.48 nm, respectively. In addition, rGO-PEDOT/PSS composite sample without DEG treatment was also characterized by XRD, with a interlayer distance (0.46 nm) slightly smaller than sample with DEG treatment, further indicating DEG’s role in increasing porosity and surface area.

3.3.2.3 Raman spectroscopy

Figure 3.6 Raman Spectra of rGO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS films

The Raman spectra of samples discussed above are shown in Figure 3.6. The signature
peaks for PEDOT/PSS at 1432 cm\(^{-1}\) (symmetric stretching of aromatic \(C=\)C band), 1535 cm\(^{-1}\) (\(C_\alpha-C_\alpha\) stretching deformation), 1372 cm\(^{-1}\) (\(C_\beta-C_\beta\) stretching deformation), 1256 cm\(^{-1}\) (\(C_\alpha-C_\alpha\) inter-ring stretching vibration), 580 cm\(^{-1}\) and 994 cm\(^{-1}\) (oxyethylene ring deformation) were also found in rGO-PEDOT/PSS composite albeit with significantly weaker intensity\(^{[29]}\). Three main peaks of rGO at 1330, 1590 and 2628 cm\(^{-1}\) associated with the D, G and 2D bands, respectively, can also be observed in the composite films. The D/G intensity ratio of the composite films increased from 1.12 (GO-PEDOT/PSS) to 1.25 (rGO-PEDOT/PSS) after HPA treatment suggesting reduction of defects in GO\(^{[33]}\). In addition, the increased 2D intensity because of the recovery of crystallinity also verified the reduction of GO\(^{[34]}\).

3.3.2.4 Fourier-transform infrared spectroscopy (FTIR)

![FT-IR Spectra of rGO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS films](image)

Figure 3.7 FT-IR Spectra of rGO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS films
The Fourier transform infrared spectra (FTIR) (Figure 3.7) corroborated the Raman results. All of the PEDOT/PSS signature peaks (S-O and S-phenyl bonds in sulfonic acid located at 1167, 1126 and 1029 cm\(^{-1}\), respectively; and C=C, C-C and C-S bonds in the thiophene backbone at 1580, 1508, 1001, 894, 771 and 706 cm\(^{-1}\), respectively) were observed in the rGO-PEDOT/PSS composite films at lower intensity\(^{[29]}\). From the comparison of GO-PEDOT/PSS and rGO-PEDOT/PSS (shown as inset), the peaks for GO at 1045 cm\(^{-1}\) and 1209 cm\(^{-1}\) (epoxy C-O stretching vibration) and 1650 cm\(^{-1}\) (associated with carboxyl group) can be seen in GO-PEDOT/PSS but not in rGO-PEDOT/PSS, indicating the reduction of GO in the composite films.

### 3.3.2.5 Thermogravimetric analysis (TGA)

![TGA curves of rGO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS films](image)

Figure 3.8 TGA curves of rGO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS films

The thermal stability of rGO-PEDOT/PSS composites in air was examined by Thermo-
gravimetric analysis (TGA). Figure 3.8 shows the comparison of weight loss of pristine rGO, pristine PEDOT/PSS and rGO-PEDOT/PSS composite. The rGO-PEDOT/PSS composite films show little weight loss below 250 °C indicating a wide operating temperature range, which is important for many applications. Above 250 °C, there was a significant mass loss, which is attributed to the rupture of the sulfonate group from PSS\cite{30}. The steepest weight loss was observed at 500 °C, which is attributed to both the degradation of the polymer backbone and the oxidation of rGO\cite{30}.

3.3.2.6 Electrical Conductivities

![Graph showing electrical conductivity of different films before and after HPA treatment.](image)

Figure 3.9 Electrical conductivity of different films before and after HPA treatment

The reduction of GO in the composites is also evident in the enhancement of electrical conductivity. Figure 3.9 shows the electrical conductivity of all films before and after reduction (HPA treatment). Electrical conductivity of PEDOT/PSS film had a negligible increase after HPA treatment (from 230.9 S cm\(^{-1}\) to 235.2 S cm\(^{-1}\)), which indicate that
HPA cannot damage the conductive polymer chains and has no influence on PEDOT/PSS’s electrical conductivity. Films containing GO (i.e., composite film and pure rGO film) show remarkable increases in conductivity after HPA treatment, indicating the reduction of GO. Among all the reduced composite films, the rGO-PEDOT/PSS film with 20 wt.%, 33 wt. %, and 50 wt.% GO loading displayed relatively high conductivity of 85.3 S cm\(^{-1}\), 92.5 S cm\(^{-1}\), and 91.3 S cm\(^{-1}\), respectively. Despite these films exhibit much lower conductivity than pure PEDOT/PSS film, the values are still comparable with literature reported flexible and conductive film electrodes.\(^{[4,35]}\) When the GO ratio is above 50\%, the conductivity decreased with GO ratio due to the relatively low conductivity of rGO film (12.1 S cm\(^{-1}\)).

3.3.2.7 Impact of HPA on PEDOT/PSS in the composites (XRD, FTIR, Raman and TGA characterization)

To ensure that PEDOT/PSS was not damaged when the composite films were treated using HPA, we also characterized the composite films before and after HPA treatment by FT-IR, Raman, XRD and TGA (Figure 3.10). The observed main peak at 2\(\theta\) = 25.9\(^{\circ}\) in the XRD pattern of treated PEDOT/PSS sample shows the retention of the (020) plane of PEDOT/PSS’s polymer backbone. In FTIR and Raman, all the signature peaks PEDOT/PSS remained the same after HPA reduction, indicating the existence of all the related functional groups and chemical bonds in reduced sample. In addition, the steepest degradation peak of PEDOT/PSS before and after HPA occurred at 500 °C due to polymer backbone rupturing, which also indicates the undamaged polymer backbone. All these results suggest that HPA is an applicable reduction agent of graphene oxide in the composite films and has no adverse impact on the PEDOT/PSS component.
Figure 3.10 Physical characterization of PEDOT/PSS before and after HPA treatment. (a) XRD, (b) TGA, (c) FT-IR and (d) Raman spectra.

3.3.3 Electrochemical performance of rGO-PEDOT/PSS device.

The rGO-PEDOT/PSS composite films with various GO loadings were prepared as illustrated in Figure 3.11. Solid-state supercapacitors were assembled by sandwiching poly(vinyl alcohol) (PVA)/H₃PO₄ solid-state electrolyte between two symmetric electrode films. The composite films displayed high flexibility and the assembled device could be bent and twisted without impairing the integrity of the device (Figure 3.11). The pristine PEDOT/PSS and pristine rGO films were also prepared using the same method for comparison. In addition, the composite films before reduction and without DEG treatment were also assembled into flexible supercapacitor for performance testing to
confirm the effective reduction of GO and the function of DEG, respectively. The active area of all fabricated solid-state supercapacitors was set at 2 cm × 0.8 cm.

**Figure 3.11** Schematic illustration of the preparation process of rGO-PEDOT/PSS films and the structure of assembled supercapacitor devices.

### 3.3.3.1 Composite devices before and after GO reduction

To further confirm the effective reduction of GO, the composite film electrodes (with 33 wt.% GO loading) before and after reduction were assembled into flexible supercapacitors. The CV curve of rGO-PEDOT/PSS (Figure 3.12a) at the scan rate of 50 mV s⁻¹ showed a great increase in the integral area compared with the unreduced one (i.e. GO-PEDOT/PSS), which indicate the enhanced double layer capacitance of composite samples after reduction. The calculated specific capacitances Figure 3.12b of electrode films also suggest that the rGO-PEDOT/PSS sample has much higher specific capacitance than the GO-PEDOT/PSS sample at scan rates, indicative the effective reduction of GO.
Figure 3.12 (a) CV curves (scan rate = 50 mV s⁻¹) and (b) specific capacitance of GO-PEDOT/PSS composite device with 33 wt.% GO before and after HPA treatment.

3.3.3.2 rGO-PEDOT/PSS devices with and without DEG

Figure 3.13 (a) CV curves (scan rate = 50 mV s⁻¹) and (b) specific capacitance of rGO-PEDOT/PSS composite device with 33 wt.% GO with and without DEG.

Comparison of CV curves and specific capacitance of the composite device with and without DEG was shown in Figure 3.13. The CV curve in the rGO-PEDOT/PSS with DEG device is more rectangular and exhibit larger integral area compared with that of rGO-PEDOT/PSS without DEG device. The specific capacitance of rGO-PEDOT/PSS with DEG device is also higher (81.7 F g⁻¹ versus 74.0 F g⁻¹ at 5 mV s⁻¹) and exhibit better
rate capability (62.2% versus 56.6% capacitance retention at 500 mV s\(^{-1}\)) than the device without DEG. The results show the positive effect of DEG on the composite film, and therefore DEG was added in all the composite samples.

3.3.3.3 Devices with varying component ratio.

The various mass loadings and thicknesses of the electrode films are presented in Table 3.1. Figure 3.14 compares the electrochemical performance of pure PEDOT/PSS, pure rGO, and rGO-PEDOT/PSS composite devices. The CV curve of pure PEDOT/PSS has excellent rectangular shape along all the scan rates from 5 ~ 500 mV s\(^{-1}\) due to the excellent good ion permeability and electrical conductivity. The composite devices also have rectangular shaped CV curves and the integral area of these curves increase with GO loadings at a low scan rate of 5 mV s\(^{-1}\). It indicates the good penetration of electrolyte ion into the inner surface of electrode materials in composite films at this scan rate. However, when the scan rate increase to 100 mV s\(^{-1}\) and higher (Figure 3.14b and c), the curves of some composite devices (i.e. with 50 wt.%, 67 wt.% and 80 wt.% GO loading) encounter great shape distortion from rectangular. Only the sample with GO loading of 20 wt.% and 33 wt.% kept their square CV curve, which indicate that the fast ion transfer was only maintained in these two samples. It was also observed that the 33 wt.% GO loading composite sample exhibit the largest CV integral area at these scan rates and consequently the highest capacitance. The main feature of rGO’s CV curves is nonrectangular at all scan rates and the CV area is smaller than those composite devices, which is resulted from the serious re-stacking problem and hydrophobic inner surface of rGO electrodes. In addition, the rGO has the lowest conductivity as shown in Figure 3.9, which leads to its slow charge-discharge response.
Table 3.1 List of mass loading and thickness of electrode films with different component ratios.

<table>
<thead>
<tr>
<th>Different films</th>
<th>PEDOT/PSS</th>
<th>rGO-PEDOT/PSS with different GO loadings</th>
<th>rGO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20%</td>
<td>33%</td>
</tr>
<tr>
<td>Mass loading (mg cm(^{-2}))</td>
<td>2.00</td>
<td>1.22</td>
<td>1.28</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>14.0</td>
<td>13.8</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Figure 3.14 CV curves of pristine PEDOT/PSS, pristine rGO and rGO-PEDOT/PSS composite (with different GO loading) devices. (a) 5 mV s\(^{-1}\), (b) 100 mV s\(^{-1}\), (c) 200 mV s\(^{-1}\) and (d) 500 mV s\(^{-1}\).
Figure 3.15 Specific capacitance of pristine PEDOT/PSS, pristine rGO and rGO-PEDOT/PSS composite (with different GO loading) devices.

The calculated electrode capacitances versus scan rates (Figure 3.15) are consistent with the observed trend from CV curves. Despite that the 80 wt.% GO sample exhibited the largest specific capacitance of 112 F g\(^{-1}\) at the lowest scan rate, the value decreased much faster than all other composite samples with lower GO loading when scan rate increased. The 33 wt.% GO loading composite electrode exhibit comparable specific capacitance at low scan rate (from 81.7 F g\(^{-1}\) at 5 mV s\(^{-1}\) to 62.8 F g\(^{-1}\) at 100 mV s\(^{-1}\)), but the highest capacitances at fast scan rate (from 60.6 F g\(^{-1}\) at 150 mV s\(^{-1}\) to 37.9 F g\(^{-1}\) at 1000 mV s\(^{-1}\)). Therefore, the composite sample containing 33 wt.% GO loading was considered to exhibit the best electrochemical performance (in terms of capacitance and charge transfer rate), and therefore was selected for further study. Notably, the gravimetric capacitance of the optimized rGO-PEDOT/PSS film in this work is only 81 F g\(^{-1}\) at the lowest scan rate of 5 mV s\(^{-1}\), which is much lower than many literature values of graphene-PEDOT.
based SCs (100–300 F g⁻¹)\(^{[36,37]}\). That is due to the limited gravimetric capacitance (28.9 F g⁻¹ even after optimized by DEG) of commercialized PEDOT/PSS utilised in this work.

To achieve the aim of industrial large-scale fabrication of rGO-PEDOT/PSS large area SCs, commercialised PEDOT/PSS was chosen instead of specially designed high performance PEDOT/PSS\(^4\) to work as flexible and conductive platform matrix for rGO sheets, which lead to the weaker performance in comparison with previous work. However, the specifically high conductivity of PEDOT-PSS utilised in this work enable the fast charge transfer in the SCs, promising the high mass loading of electrode materials which resulted high areal capacitance.

Table 3.2 Calculated specific capacitance of rGO (C\(_g\)) in the composite film based on the mass of rGO and Equation 3.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P(_g)</th>
<th>P(_p)</th>
<th>C (F g(^{-1}))</th>
<th>C(_g) (F g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% GO</td>
<td>20%</td>
<td>80%</td>
<td>68.7</td>
<td>227.9</td>
</tr>
<tr>
<td>33% GO</td>
<td>33%</td>
<td>67%</td>
<td>81.68</td>
<td>188.8</td>
</tr>
<tr>
<td>50% GO</td>
<td>50%</td>
<td>50%</td>
<td>87.2</td>
<td>145.5</td>
</tr>
<tr>
<td>67% GO</td>
<td>67%</td>
<td>33%</td>
<td>98.54</td>
<td>132.8</td>
</tr>
<tr>
<td>80% GO</td>
<td>80%</td>
<td>20%</td>
<td>110.65</td>
<td>131.1</td>
</tr>
<tr>
<td>rGO</td>
<td>100%</td>
<td>0%</td>
<td>56.11</td>
<td>56.11</td>
</tr>
</tbody>
</table>

\[ C\(_g\) \times P\(_g\) + C\(_p\) \times P\(_p\) = C \]  

Equation 3.1

Since most of the capacitance derives from EDLC-type rGO, gravimetric capacitances of rGO (C\(_g\)) in the composite films were calculated according to Equation 3.1, where C and C\(_p\) is the gravimetric capacitance of the composite electrode and pristine PEDOT/PSS at
5 mV s\(^{-1}\) respectively, \(P_g\) and \(P_p\) is the mass percentage of GO and PEDOT/PSS in composite film. It can be seen that \(C_g\) in composite (33 wt. % GO loading) is 189 F g\(^{-1}\) (Table 3.2), while the capacitance of pure rGO film is only 56.11 F g\(^{-1}\). This can be explained to be the result of effective prevention of rGO’s restacking problem by the addition of PEDOT/PSS. In addition, the higher loading of PEDOT/PSS in the composite resulted in higher \(C_g\), which indicated that high PEDOT/PSS loading can effectively prevent the re-stacking of rGO sheets.

Figure 3.16 Ragone plots of pristine PEDOT/PSS, pristine rGO and rGO-PEDOT/PSS composite (with different GO loading) devices.

There is also the same trend in the power and energy densities (based on two electrode weights, calculated from CV data), which can be observed from the Ragone plot in Figure 3.16. The device containing optimal rGO-PEDOT/PSS electrode (33 wt.% GO loading)
can achieve a maximum power and energy densities (3,589.5 W kg$^{-1}$ and 2.83 Wh kg$^{-1}$, respectively), which are significantly higher than devices made of pure rGO electrode (159.8 W kg$^{-1}$ and 1.95 Wh kg$^{-1}$, respectively) and pure PEDOT/PSS electrode (1,967.5 W kg$^{-1}$ and 1.00 Wh kg$^{-1}$, respectively).

Figure 3.17 Nyquist plots of pristine PEDOT/PSS, pristine rGO and rGO-PEDOT/PSS composite (with different GO loading) devices.

Figure 3.17 shows the Nyquist plot comparison of devices made from pure rGO, pure PEDOT/PSS and rGO-PEDOT/PSS electrodes. It can be seen that, in the low frequency regime of all plots, the imaginary part of impedance increased rapidly and tend towards a vertical line, which is the characteristic of capacitive behaviour. In the high frequency region (inset in Figure 3.17), a small semi-circle can be observed in all samples, the size of which defines the charge transport resistance. The PEDOT/PSS device shows the smallest semi-circle while the rGO device exhibits the largest one. In the composite devices, the semi-circle size increases with the initial GO loading. These results indicate
that the existence of rGO increase the charge transport resistance in the composite devices and therefore affect the ion diffusion rate, which is consistent with the results from CV curves.

Figure 3.18 Galvanostatic charge/discharge curves of rGO-PEDOT/PSS (33 wt.% GO) at different current densities, with inset of the calculated specific capacitance.

The symmetry of the galvanostatic charge/discharge curves Figure 3.18 of the rGO-PEDOT/PSS signifies the excellent capacitive characteristic, with the discharge time decreasing with increasing the applied current, leading to a slight decrease in specific capacitance (inset in Figure 3.18). No significant iR drop is observed at the beginning of the constant current discharge, indicative of the low contact resistance in the device. The calculated specific capacitance is consistent with the values from CV curves.
Figure 3.19 (a) Capacitance and coulombic efficiency of rGO-PEDOT/PSS (33 wt.% GO) device during the 20,000 cycles and (b) Nyquist plot of rGO-PEDOT/PSS (33 wt.% GO) device prior to and after 10,000 and 20,000 cycles.

The long-term charge-discharge performance of this device was also evaluated (Figure 3.19a). After 10,000 cycles of constant current charge/discharge at 1 A g\(^{-1}\), the capacitance retention was more than 95 %. When tested for another 10,000 charge/discharge cycles at a higher current density of 2 A g\(^{-1}\), the capacitance remained above 85 % of the initial value, suggesting that the device has high stability, long cycle life, and high rate capability. The Coulombic efficiency is also close to 100 % for all cycles indicating the high stability of the device. This high stability is also shown in the Nyquist plots (Figure 3.19b). A slight decrease in semi-circle of the high frequency region after 10,000 and 20,000 charge/discharge cycles demonstrates decreased polarisation resistance (R\(_{ct}\)). In addition, the intercept of the real part of impedance with the x-axis (R\(_s\), representative of the resistance of the electrolyte and the contact resistance) also decreased slightly. These results suggest that the inner surface of electrode materials has been fully wetted by the electrolyte after 10,000 cycles with only a minimal mechanical failure from the polymer doping/dedoping and ion absorbing/desorbing process\(^{38,39}\).
3.3.3.4 rGO-PEDOT/PSS devices with different thicknesses

It has been reported that thin electrode films often lead to better specific capacitance performance because electrons and electrolyte ions can be easily transferred. However, in most practical applications, high mass loading and hence film thickness is necessary to increase device capacity. Here, devices with various electrode material mass loading were fabricated to investigate the relationship between mass loading and specific (i.e. areal, volumetric and gravimetric) capacitance of the PEDOT/PSS-rGO composite electrode with 33 wt. % GO loading. As shown in Figure 3.20, the areal capacitance increases with mass loading initially before reaching the highest value of 448 mF cm$^{-2}$ at 8.49 mg cm$^{-2}$ at a scan rate of 10 mV s$^{-1}$. This performance is comparable with previously reported values for graphene (Laser scribing graphene (LSG)\cite{40}, Graphene-Cellulose nanofiber (G-CN) aerogel\cite{18}, and Graphene-cellulose paper\cite{41}), CNT\cite{9,41} and conducting polymer\cite{5} solid-state SCs. The gravimetric capacitance at this loading is 52.7 F g$^{-1}$. Also, the volumetric capacitance (49.9 F cm$^{-3}$) is higher than reported values for solid state graphene (9.6 F cm$^{-3}$\cite{40}, graphene hydrogel (31 F cm$^{-3}$\cite{42} and PEDOT paper (35 F cm$^{-3}$)\cite{43}. In addition, the volumetric capacitance (3.4 F cm$^{-3}$) of the whole SC device (i.e. taking into account the mass of the 0.66 mm thick electrode, electrolyte and package membranes) is significantly higher than previous reports CNT (0.30 F cm$^{-3}$\cite{44}, and graphene (0.42 F cm$^{-3}$\cite{7}, and comparable with PEDOT-paper (5 F cm$^{-3}$)\cite{43}. At a high scan rate of 100 mV s$^{-1}$, the device with 8.49 mg cm$^{-2}$ mass loading can retain an areal capacitance of 300 mF cm$^{-2}$, indicating good rate capability. The CV curves encounter some distortion from rectangular at a higher scan rate of 100 mV s$^{-1}$, but the device with 8.49 mg cm$^{-2}$ mass loading electrodes still exhibit high areal capacitance of 302 mF cm$^{-2}$, comparable gravimetric and volumetric capacitance of (35.6 F g$^{-1}$ and 35.3
F cm\textsuperscript{3}). This indicates the good rate capability of this high mass loading device.

Figure 3.20 Dependence of the electrochemical properties of supercapacitor on electrode mass loading. (a) CV curves at 10 mV s\textsuperscript{-1}, (b) Areal, volumetric and gravimetric capacitance versus thickness at a scan rate of 10 mV s\textsuperscript{-1}. (c) CV curves at 100 mV s\textsuperscript{-1}, (d) Areal, volumetric and gravimetric capacitance versus thickness at a scan rate of 100 mV s\textsuperscript{-1}.

The symmetric galvanostatic charge/discharge curves (Figure 3.21a) under different current densities signified good capacitive characteristic. The device delivers an energy density of 34 μWh cm\textsuperscript{-2} (Figure 3.21b), which is higher than G-CN aerogel SC (20 μWh cm\textsuperscript{-2}) \cite{18}, Graphene hydrogel SC (25.8 μWh cm\textsuperscript{-2}) \cite{42}, Graphene cellulose paper SC (2 μWh cm\textsuperscript{-2}) \cite{41} and PEDOT paper SC (17 μWh cm\textsuperscript{-2}) \cite{43}. It was also found that the
flexibility of the device was not affected by the increase of electrode film thickness.

Figure 3.21 Electrochemical performance of rGO-PEDOT/PSS (33 wt.% GO) device with the high mass loading of 8.489 mg cm$^{-2}$. (a) Charge-discharge curves and (b) Ragone plot.

3.3.4 Flexibility and Durability of fSSCs.

Cyclic voltammetry (CV) (Figure 3.22a) and the charge/discharge curves (Figure 3.22c) confirm that no significant change was observed during bending at various angles. Bending up to 1,000 times at 180 ° did not change the shape of the CV responses (Figure 3.22b). The long term galvanostatic tests illustrated that the capacitance tested under 180 ° after 10,000 cycles only decreased by 11.6 % compared with 0 °, indicating excellent device performance under large bending angles (Figure 3.22d). In addition, the SC device made from a long strip of electrodes (15 cm × 2 cm) that have been rolled-up as shown in Figure 3.22e and f was powerful enough to power a light-emitting diode for 20 seconds when fully charged (Figure 3.22g).
Figure 3.22 (a) CVs of rGO-PEDOT/PSS during bending. Scan rate = 50 mV s⁻¹. (b) CVs of rGO-PEDOT/ PSS after being subject to bending. (c) Charge-discharge curves of rGO-PEDOT/PSS during bending. (d) Long-term test of rGO-PEDOT/PSS under flat or 180 degree bended states at a current density of 1 A g⁻¹. (e) Flexible films coated with solid electrolyte spread out on an Au- coated membrane, (f) rolled design and (g) the resulting device used to power a green light-emitting diode (LED).
3.4 Conclusion

In summary, highly flexible free-standing rGO-PEDOT/PSS films have been successfully prepared and fabricated into flexible all-solid-state SC devices using PVA/H₃PO₄ as an electrolyte. The incorporation of PEDOT/PSS and DEG into GO sheets increased the interlayer spacing of GO sheets and prevented the GO sheets from re-stacking, which significantly improved the electrochemical performance of the assembled SCs, created more effective surface area and improved the penetration of large sized solid electrolyte ions into the electrode materials. The GO in composite films can be reduced effectively using HPA as the reducing agent, which was verified by FTIR, Raman and XRD and electrical conductivity measurements. The maximum areal capacitance (448 mF cm⁻²) was obtained using 33 % rGO-PEDOT/PSS electrode film with 8.49 mg cm⁻² loading at a scan rate of 10 mV s⁻¹. Notably, this composite material performed better than previous reports and showed little changes in capacitance when bent at various angle for 1,000 times. This excellent performance and the ease of fabrication suggest that such electrode materials are good candidates for bendable SC devices that are practical for large scale use.

3.5 Reference


Chapter 4  Laser Fabrication of Flexible Microsupercapacitors with Interdigitated Electrodes

This chapter is adapted from the article, “Facile Fabrication of Flexible Microsupercapacitor with High Energy Density”, by Yuqing Liu, Bo Weng, Qun Xu, Yuyang Hou, Chen Zhao, Stephen Beirne, Keiwei Shu, Rouhollah Jalili, Gordon G. Wallace, Joselito M. Razal, and Jun Chen” that was published in Advanced Materials Technologies (2016, 1600166). Adapted with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
4.1 Introduction

Flexible microsupercapacitors (fMSCs) are being studied extensively as alternative power source for flexible and wearable electronics. However, achieving outstanding performance, which are the combination of high energy density, high power density, fast charging and discharging rates for extended periods (>10,000 cycles) and high stability, is proven to be still a challenge.\textsuperscript{[1–4]} Specifically, fMSCs that are constructed using a conventional design (\textit{i.e.} two planar electrodes facing each other separated by electrolyte) display performance that fall short of the requirements of microelectronics.\textsuperscript{[5–7]} To enhance device performance, fMSCs that employ an interdigitated layout of active electrodes have been investigated recently aiming at providing better interaction between electrolyte and electrode materials. This design can generate more ion-accessible surface area between electrolyte and electrode materials, which allows ions in electrolyte to permeate into electrode materials more easily.\textsuperscript{[8–10]} Compared with the conventional sandwiched construction, this new design provides the opportunity for attaining higher energy and power densities from a limited space through the control of the dimensions and arrangement of the interdigitated micro-fingers. This design also allows planar interconnection between several devices without the intricate connections of wires.\textsuperscript{[11]} However, present fMSCs with interdigitated electrode design require careful choice of electrode material and sophisticated fabrication techniques for electrode patterning.\textsuperscript{[12,13]}

The energy density of fMSCs, which are evaluated by the areal and volumetric capacitance of the whole device, relies on the quality of electrode materials.\textsuperscript{[14]} Recent efforts have focused on using carbon nanomaterials due to their low-cost, excellent electrical conductivity and long-cycle life.\textsuperscript{[2,9,10,15–17]} Among these nanomaterials, single
layer graphene shows superior volumetric and areal capacitance (600 F cm\(^{-3}\) and 21 µF cm\(^{-2}\), respectively) because of its large surface area (2620 m\(^2\) g\(^{-1}\))\(^{[18,19]}\). Other graphene derivatives used in fMSCs such as graphene quantum dots\(^{[15]}\), reduced graphene oxide (rGO)\(^{[11,20,21]}\), heteroatom-doped graphene\(^{[22]}\) also display high volumetric capacitance (15 to 100 F cm\(^{-3}\)) but low areal capacitance (80 - 500 µF cm\(^{-2}\)) because of the relatively thin electrodes employed (8 - 300 nm). It is typically observed for graphene electrodes that volumetric capacitance does not scale with electrode thickness because of the re-stacking of individual graphene sheets and insufficient utilization of their surface area. Other forms of nanostructured carbons like onion-like carbon\(^{[2]}\), porous activated carbon\(^{[16]}\), rGO-carbon nanotubes(CNTs)\(^{[17]}\) and porous graphene\(^{[13]}\) also provide high ion-accessible surface area, low packing density, and improved areal capacitances (0.2 - 13 mF cm\(^{-2}\)) but the volumetric capacitance is lower (1 - 7 F cm\(^{-3}\)). Some pseudo-capacitive materials like PANi\(^{[12,23]}\) and metal oxides\(^{[24]}\) have been used to increase volumetric capacitance (>50 mF cm\(^{-2}\) and >20 F cm\(^{-3}\), respectively) but the capacity retention and cycling stability are poor (≤90% at 1,000 cycles) due to the redox involved during the charging and discharging process. To date, however, it is still a challenge to prepare a sub-micrometer thick fMSC electrode with good ion accessibility and high packing density that can deliver both high areal and volumetric capacitance, and exhibit high capacitance retention for extended cycle.

The scalable fabrication of patterned electrodes is another limitation for fMSCs. Lithography can make elaborate electrode patterns but cost can be very high for mass production.\(^{[2,11,12,15,17,20–24]}\) Recently, several groups have used laser printing as a writing tool to directly pattern graphene micro-electrodes on its precursor film (e.g. GO\(^{[13,25]}\) and polyimide sheets\(^{[26,27]}\)), demonstrating a fast and simple technique for fabricating fMSCs.
El-Kady et. al. described a scalable fabrication of graphene fMSCs by direct laser writing on GO films using a standard LightScribe DVD burner, printing more than 100 MSCs on a single disc in 30 minutes.\(^\text{13}\) One challenge in the aforementioned approach is that residual precursors are left in between the micro-electrodes, which affect the electrolyte penetration from the lateral side of the microelectrodes and result in decreased ion diffusion rate. Recently, laser lithography technology (known as laser-cutting system) was also used as an etching tool to create patterned channels on various kinds of film electrodes (MoS\(_2\)^{28}, aMP\(^{29}\) and MDC\(^{30}\)). It is believed that this technology can be applied to a range of electrode materials and film thicknesses provided that residual precursors (or any unwanted materials) are completely removed to create well-separated microelectrodes. This fiber-laser cutter “etches” unwanted material away from the electrode as opposed to “writing” the electrode to generate any practical MSC electrode design on the substrate. The simplicity of this technology (i.e. computer-generated intricate patterns can be “written” on any materials, which include polymers, nanomaterials and many others, and substrates of complex shapes and structures) can pave the way to rational engineering of novel materials for related wearable electronic devices not limited to energy storage applications.

We have developed a scalable large-size, conductive and flexible film based on rGO-PEDOT/PSS in Chapter 3, which exhibit high packing density and good ion accessibility in thick films. In this chapter, we modified the film preparation process and developed an fMSCs with superior electrochemical performance by using a facile laser etching process to achieve an interdigitated pattern on the flexible rGO-PEDOT/PSS film. The PEDOT/PSS component was effectively stacked in between graphene sheets forming a densely-packed composite electrode (1.4 g cm\(^{-3}\)), which made it possible to develop
fMSCs with excellent areal (84.7 mF cm\(^{-2}\) at 5 mV s\(^{-1}\) and 45.5 mF cm\(^{-2}\) at 200 mV \(^{-1}\)) and volumetric capacitance (14.5 F cm\(^{-3}\) at 5 mV s\(^{-1}\) and 7.83 F cm\(^{-3}\) at 200 mV \(^{-1}\)), as well as good cycling stability (94.3% capacitance retention after 10,000 cycles). Up to ten interdigitated electrode patterns can be achieved within just 100 seconds, demonstrating a very fast patterning process. The electrode patterns, dimensions and interconnects can be easily adjusted by varying the laser etching parameters in order to achieve the desired energy, power, current and voltage. Furthermore, a long strip of flexible device with 12 tandem fMSCs was demonstrated to power 20 light emitting diodes (LEDs).

4.2 Experiment

4.2.1 Preparation of rGO-PEDOT/PSS dispersions and films

rGO-PEDOT/PSS dispersions were prepared by reducing GO under the presence of PEDOT/PSS in the dispersion (GO-PEDOT/PSS dispersion). Firstly, PEDOT/PSS pellets were added into GO dispersions (prepared by improved Hummers method),\(^{[34,55]}\) stirred overnight and then sonicated for 30 minutes (Branson B5500R-DTH bath sonicator). Samples with various GO loadings of 20 wt.%, 33 wt.%, 50 wt.%, 67 wt.% and 80 wt.% were prepared. In each sample, the total concentration (solid content) of PEDOT/PSS and GO was kept at 15 mg mL\(^{-1}\). HPA (reduction agent) was added into the as-prepared GO-PEDOT/PSS dispersion at GO:HPA of 1:20 by weight, stirred at 90 °C for 5 hours, and then dialyzed for 3 days to remove the residual acid. Diethylene glycol was added into the obtained rGO-PEDOT/PSS dispersion at a DEG:solid content weight ratio of 1.86:1. Pure rGO dispersion was also prepared using the same method for comparison.
rGO-PEDOT/PSS films were prepared by bar-coating a thin layer of rGO-PEDOT/PSS dispersion on a 100 nm Au sputter coated PET plastic film (100 µm thickness) to a fixed shape and size as described in Chapter 2.3.1.1.1. The film’s thickness was controlled by the volume of dispersion used per unit area of the film.

**4.2.2 Fabrication of rGO-PEDOT/PSS fMSCs**

rGO-PEDOT/PSS fMSCs were produced by direct laser cutting on rGO-PEDOT/PSS films as illustrated in Figure 4.1 and described in Chapter 2.3.1.2

**4.3 Results and Discussions**

**4.3.1 Feasibility of fabricating rGO-PEDOT/PSS flexible micro-supercapacitors via laser-etching method.**

**4.3.1.1 Fabrication of all-solid-state rGO-PEDOT/PSS-based fMSC using laser-cutter.**

Figure 4.1 shows the fabrication process of the all-solid-state fMSCs. Briefly, an rGO-PEDOT/PSS dispersion was bar coated onto an Au sputter-coated PET sheet and then dried. A CO₂ laser cutter system was used to achieve the desired interdigitated patterns by etching the unwanted components (creating channels) and only leaving the active electrode component intact and adhered onto the substrate. Planar fMSCs were made and tested after receiving an electrolyte overcoat. Compared with photolithography\(^{[23,31]}\) and wet-etching methods\(^{[12,20,32]}\), the overall fMSC fabrication process is simpler, quicker, and potentially lower in cost. The laser etching parameters are easily adjustable to achieve
various micron resolution patterns without post-processing and therefore readily scalable. For example, ten fMSC devices with different pattern dimensions (i.e. increasing number of electrode fingers ($N$), denoted as fMSC($N$) in Figure 4.2a) can be readily prepared in just 100 seconds during a single laser etching run on a 5 cm × 7 cm substrate.

![Figure 4.1 Schematic diagram of the fabrication of all-solid-state rGO-PEDOT/PSS-based planar fMSCs on a flexible PET film using laser cutter technique](image)

There are a number of factors that were expected to influence the performance of interdigitated fMSCs, which include not only the composition of the active electrode material, but also the electrode design and dimensions such as the distance between adjacent fingers ($d$), the finger width ($W$) and length ($L$) etc. It has been reported that narrow $d$ results in increased capacitance and rate capability because this design enables simultaneous maximization of active material loading and minimization of ion diffusion pathway between the two oppositely charged electrodes (i.e. anode and cathode). In our case, an interdigitated electrode pattern with the lowest $d$ of \(~100\ \mu\text{m}\) can be achieved.
without shorting the circuit as shown in Figure 4.2b; this resolution is similar to previously reported MSCs.\textsuperscript{[2,26,27,29,33]} In addition, a small \( W \) of \( \sim 400 \, \mu \text{m} \) can also be observed in the fMSC(20) pattern, which represents \( \sim 83 \% \) utilization of the available active electrode area compared to full utilization for non-patterned \((i.e.\ flat)\) electrode.

Figure 4.2 (a) Photo images of laser-etched fMSCs with different configurations on one rGO-PEDOT/PSS film. (b) SEM image of fMSC (20) pattern (top view)

4.3.1.2 \textbf{Flexibility and Durability fMSCs.}

Shown in Figure 4.3a is the digital image of a fabricated all-solid-state fMSC(20) device during bending and Figure 4.3b displays how a manually bent fMSC(20) device maintained its integrity. To prove the bendability endurance of fMSCs, the electrochemical performance of fMSC(20) was tested under flat and various bending conditions. Figure 2b shows the CV curves when the device was bent at various curvatures. It can be seen that there is a negligible change in the CV curves when the device was repeatedly bent from \( L=1 \, \text{cm} \) to \( L=0 \, \text{cm} \) for up to 1,000 times indicating the fMSC device’s excellent performance durability.
Figure 4.3 (a) Photograph of assembled fMSC device on its bent state. (b) Comparison CVs of the fMSC device before (L = 1 cm) and after bending at different curvatures (L = 0.8, 0.5, 0.2, and 0 cm). Also shown is the CV after repeatedly bending the fMSC device from L = 1 to L = 0 for 1000 times.

4.3.1.3 Connection between fMSCs.

Some applications require current or voltage that is higher than what can be delivered by a single supercapacitor device. One way to meet this requirement is to electrically connect these supercapacitors in series, in parallel or a combination of these connections. Here, these interconnects were readily achieved using the same laser etching method used for a single fMSC device. As shown in Figure 4.4, four fMSC(20) devices were connected in series, in parallel, and a combination of these two by simply changing the etching circuit to form the desired patterns without additional wires for circuitry. The output current of the parallel configuration increased by a factor of four compared with a single fMSC(20) (Figure 4.4a), and a widened voltage window of 4 V can be easily achieved by connecting four fMSCs(20) in series (Figure 4.4b). A combination of two series and two parallel connections enhanced the voltage range to 2 V without decreasing the output current.
These results indicate that the laser-formed tandem connections between fMSCs enable good control over operating window and current densities. In addition to the ease of fabrication process, the laser-etched fMSCs show great promise for real world applications.

![Figure 4.4 CVs (scan rate = 100 mV s⁻¹) for four microsupercapacitors connected (a) in parallel, (b) in series, and (c) in a combination of series and parallel.](image)

The above results proved the feasibility of scalable fabrication of single and tandem fMSCs via laser-etching technique; Therefore, the next step is to optimize detailed parameters (i.e., in both electrode materials and device parameters) for better application. To improve the device performance, the quality of flexible electrode films plays a significant role.

**4.3.2 Physical Characterization of rGO-PEDOT/PSS film.**

**4.3.2.1 Photo and SEM images of the prepared composite film.**

The flexible electrode films were prepared directly from rGO-PEDOT/PSS dispersions with different component ratios. The method we used was different from our previous method used in Chapter 3 where films were prepared by first bar coating GO-PEDOT/PSS dispersion onto a substrate and the resulting film then treated chemically to reduce the
GO component into rGO.\textsuperscript{[34]} A change in method was found necessary because films made by the previous method could be easily delaminated from the substrate and was prone to flaking off during the laser etching process. In contrast, the new method of making rGO-PEDOT/PSS films (\textit{i.e.} GO was chemically reduced prior to bar coating) resulted in highly flexible films that can be bent and twisted without breaking, delaminating or flaking off the substrate (Figure 4.5). The packing density of the composite film increased from \( \sim 1.0 \) g cm\(^{-3} \) to \( \sim 1.4 \) g cm\(^{-3} \) compared to the film prepared in Chapter 3, which is beneficial for achieving high volumetric performance. The density achieved for a thick flexible electrode reported here is comparable with literature reported densities for thin film electrodes with high volumetric capacitance (1.33 ~ 1.67 g cm\(^{-3} \)).\textsuperscript{[12,35]} The cross-sectional SEM images of the interface between the bar-coated active electrode materials and the PET substrate showed excellent adhesion between the two materials (Figure 4.6). The SEM images of the film cross-sections showed that rGO sheets were densely stacked reminiscent of rGO papers but with PEDOT/PSS intercalated in between rGO sheets (Figure 4.7a). It is perceived that the PEDOT/PSS have prevented re-stacking of rGO sheets during the reduction process and the subsequent film formation. Based on SEM observations of the edges of the laser-cut rGO-PEDOT/PSS film, the edges remained open and porous similar to its parent (non-laser-cut) film (Figure 4.7). This structure suggests that electrolyte can penetrate from the exposed sides of each electrode finger in addition to the conventional electrolyte access from the basal plane of non-patterned electrodes.
Figure 4.5 Large-size flexible rGO-PEDOT/PSS film which can be bent and twisted at any angle.

Figure 4.6 Cross-sectional SEM images of the interface between rGO-PEDOT/PSS film and the PET substrate
4.3.2.2 Stability of rGO-PEDOT/PSS dispersion

The presence of PEDOT/PSS in the composite dispersion played an important role in preventing rGO from aggregation during its reduction. This effect is similar to previous observations when chemical reduction of GO is carried out in the presence of surfactant stabilizers or polymers.\textsuperscript{36–38} PEDOT/PSS, a water dispersible conducting polymer, is also known to have non-covalent $\pi-\pi$ interactions between the aromatic rings and the basal planes of graphene sheets and could serve as stabilizer for rGO sheets.\textsuperscript{39} Here we found that when GO sheets were chemically reduced in the presence of PEDOT:PSS, aggregate-free dispersions were observed at GO loadings below 50 wt. %. Upon dilution of the reduced dispersions, aggregates were present only in composite dispersions containing 67 wt. % and 80 wt. % GO loadings (Figure 4.8). The dispersions with 50 wt. % loading and below remained homogeneous and stable for one month after reduction.
Figure 4.8 Photographs of diluted rGO-PEDOT/PSS dispersions with different GO loadings.

4.3.2.3 X-ray diffraction (XRD)

Figure 4.9 XRD spectra of pure rGO, GO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS
The XRD results showed that PEDOT/PSS intercalated between the GO sheets and prevented it from re-stacking. In Figure 4.9, distinct peaks at $2\theta = 9.26^\circ$ and $2\theta = 7.9^\circ$ were found in GO and GO-PEDOT/PSS samples. These peaks are related to the (002) diffraction of graphene sheet, from which the interlayer $d$ spacing values have been calculated to be 0.95 nm and 1.12 nm according to Bragg’s law (Equation 2.1).\textsuperscript{[40]} This slight increase of interlayer spacing in GO-PEDOT/PSS composite film could be attributed to the intercalation of PEDOT/PSS in between GO layers.\textsuperscript{[41]} After reduction, the specific GO peaks at around $10^\circ$ disappeared in both rGO and rGO-PEDOT/PSS samples and broad peaks were observed at around $2\theta = 23.6^\circ$ and $2\theta = 20.0^\circ$, which corresponded to decreased interlayer distance of 0.37 nm and 0.44 nm, respectively compared with samples before reduction. The higher interlayer spacing of the composite sample than pure rGO sample also proved the good interaction of PEDOT/PSS with individual graphene sheets and its important role in preventing rGO from aggregation during its reduction. This is consistent with the cross-sectional SEM observations.

### 4.3.2.4 Raman spectra

![Figure 4.10 Raman spectra of pure rGO, PEDOT/PSS, GO-PEDOT/PSS and rGO-PEDOT/PSS samples.](image)
As mentioned in Chapter 3, the commercially sourced PEDOT/PSS we use only acts as the conductive and flexible matrix to prevent re-stacking or rGO layer and most of the capacitance arises from the rGO component of the composite electrode. Thus, effective reduction of the GO to rGO component is essential. We verified this reduction by Raman. Pristine PEDOT/PSS pellets, GO, GO-PEDOT/PSS and rGO-PEDOT/PSS dispersions were investigated by Raman spectra and shown in Figure 4.10a. The signature peaks for PEDOT/PSS (437, 576, 988, 1256, 1368, and 1428 cm\(^{-1}\)) can be observed in the rGO-PEDOT/PSS sample\(^{[42]}\) and the three main peaks of rGO at 1323, 1585 and 2624 cm\(^{-1}\) stand for the D, G, and 2D bands, respectively, can also be found in this composite sample. The D/G intensity ratio of the composite samples increased from 1.10 (GO-PEDOT/PSS) to 1.24 (rGO-PEDOT/PSS) after HPA treatment suggesting reduction of defects in GO (Figure 4.10b).\(^{[43–48]}\) In addition, the increased 2D intensity attributed to the recovery of crystallinity also verified the reduction of GO.\(^{[47,48]}\)

**4.3.2.5 X-ray photoelectron spectroscopy (XPS)**

This is also confirmed by XPS spectra of GO-PEDOT/PSS and rGO-PEDOT/PSS films (Figure 4.11). The C 1s XPS spectrurn corresponding to carbon atoms indiffert oxygen-functional groups: C-O and C=O (between 286 eV and 288 eV) exhibits much smaller intensities of these components in the reduced samples (rGO-PEDOT/PSS), clearly indicating the reduction of graphene oxide in the composite film.
4.3.3 Electrochemical performance of fMSCs.

4.3.3.1 rGO-PEDOT/PSS fMSCs before and after reduction

The enhancement of electrical conductivity and electrochemical performance also confirmed the reduction of GO in the composites. To confirm this, pristine PEDOT/PSS and GO-PEDOT/PSS film (with 33 wt. % GO loading, 3 mg cm$^{-2}$) were prepared, laser patterned and assembled into all-solid-state fMSC(20) devices in the same process as rGO-PEDOT/PSS film and fMSC(20) and performance evaluated. After reduction, the
electrical conductivity increased from 57.7 S cm$^{-1}$ for GO-PEDOT/PSS to 82.8 S cm$^{-1}$ for rGO-PEDOT/PSS film. The fMSC device (i.e., prepared using the rGO-PEDOT/PSS film with 33 wt.% GO loading) showed remarkable increase in capacitance compared to GO-PEDOT/PSS counterparts (Figure 4.12a). When compared to neat PEDOT/PSS fMSC(20), the rGO-PEDOT/PSS fMSC(20) device with the initial GO loading of only 33 wt.% can deliver increased capacitance by a factor of two. These results verified the dominant contribution of rGO towards device capacitance. In addition, the rGO-PEDOT/PSS fMSC (20) device shows much smaller equivalent series resistance (derived from the intercept of the real part of impedance with the x-axis in Nyquist plot) and charge-transport resistance (defined by the size of the semi-circle at high frequency domain in Nyquist plot) than those of GO-PEDOT/PSS fMSC (20) device (Figure 4.12b). The results show the effective reduction of GO in the composite films.

Figure 4.12 Electrochemical performance comparison of fMSCs based on composite film with 33 wt.% GO loading before and after reduction. (a) Areal Capacitance calculated from CV curves, and inset is the CV curves at the scan rate of 50 mV s$^{-1}$. (b) Nyquist plot.
The device performance of fMSC(20) was compared with a planar supercapacitor prepared from similar electrode/electrolyte composition, thickness and dimensions. This planar supercapacitor was constructed using a conventional sandwiched design where two non-patterned rGO-PEDOT/PSS films (11.6 µm-thick, 1 cm × 1 cm for each film) face each other and are separated by the PVA/H₃PO₄ gel electrolyte (Detailed dimensions in Table 4.1). We found a striking difference in performance in favor of the fMSC(20) in terms of volumetric capacitance (Figure 4.13). Without the separator layer, the device with interdigitated design is much thinner (11.7 µm) than device with sandwiched design (156 µm). Benefiting from this, interdigitated device can deliver much higher current densities and volumetric capacitance than those of the sandwiched device based on the volume of the whole device. This result shows the interdigitated design of supercapacitor can supply higher power density for microelectronics than the conventional sandwiched design.

It was not straightforward to evaluate the performance of electrode materials from capacitance based on area or volume of device because even when the two devices were produced from the electrode film of the same size, the dimension of the assembled device and the active material loading are different (Table 4.1). Therefore, we also calculated the specific capacitance based on the volume and area of electrode materials. As shown in Figure 4.14, the electrodes in interdigitated design have slightly higher areal capacitance, volumetric capacitance and rate capability than that of the electrode in the sandwiched design. These results show favorable fMSC electrode materials for electrolyte penetration and ion diffusion.
Table 4.1 Dimensions comparison between Sandwiched and Interdigitated designs.

<table>
<thead>
<tr>
<th></th>
<th>Sandwiched design</th>
<th>Interdigitated design</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode thickness</strong></td>
<td>11.6 µm</td>
<td>11.6 µm</td>
</tr>
<tr>
<td><strong>Film mass loading</strong></td>
<td>2 mg cm(^2)</td>
<td>2 mg cm(^2)</td>
</tr>
<tr>
<td><strong>Device thickness</strong></td>
<td>11.7 µm</td>
<td>156 µm</td>
</tr>
<tr>
<td><strong>Device area</strong></td>
<td>1 cm × 1 cm</td>
<td>1 cm × 1 cm</td>
</tr>
<tr>
<td><strong>Active materials loading per device</strong></td>
<td>1.664 mg</td>
<td>4 mg</td>
</tr>
</tbody>
</table>

Figure 4.13 Performance comparison between fSSC and fMSCs (a) CV curves at the scan rate of 100 mV s\(^{-1}\). (b) Volumetric capacitances calculated from CVs.
Figure 4.14 Performance comparison between fSSC and fMSC. (a) Volumetric and (b) areal capacitance of electrode.
4.3.3.3 Evaluation of composite ratio on the performance of fMSCs.

Figure 4.15 Electrochemical performance comparison of fMSCs based on rGO-PEDOT/PSS films with different GO mass loadings. (a) CVs at 10 mV s\(^{-1}\), (b) CVs at 500 mV s\(^{-1}\), (c) CVs at 1000 mV s\(^{-1}\), and (d) calculated specific capacitances vs scan rates.

The composition of rGO and PEDOT/PSS in the composite films was firstly optimized for fMSC(20) devices (mass loading of 3 mg cm\(^{-2}\)). rGO-PEDOT/PSS fMSC(20) devices with 20 wt.%, 33 wt.%, 50 wt.%, 67 wt.%, 80 wt.% GO loadings were examined and denoted as 20 wt.%, 33 wt.%, 50 wt.%, 67 wt.% , 80 wt.% respectively. We note that pure rGO-based fMSC cannot be prepared due to the poor rGO dispersible ability that cracks and flakes off easily from the substrate when cast into films. The device was evaluated using cycling voltammetry (CV) as a function of scan rate (from 5 mV s\(^{-1}\) to 5000 mV s\(^{-1}\)) and a voltage window of 1 V (Figure 4.15). At the slow scan rate of 5 mV s\(^{-1}\), the CV
curves show excellent rectangular shaped for all devices, and the CV area increases with GO weight loading. It indicates that the electrolyte ions had good access to the interior surface of the active materials at this scan rate. When the scan rate increases, the shape of CV curves began to encounter distortion from rectangular. At high scan rates of 500 and 1000 mV s\(^{-1}\), 67 wt.% and 80 wt.% fMSCs show great distortion from rectangular shape, while 20 wt.%, 33 wt.% and 50 wt.% device can maintain their square shape. Notably, the 50 wt.% device exhibit the largest area in CV curves at the high scan rates, indicating its superiority to other devices in terms of both capacitance and rate capability. The observed trend for the scan rate dependence of device capacitance on composite ratio was also true for the areal capacitance of the whole device. Therefore, we conclude that the best electrochemical performance (in terms of capacitance and charge transfer rate) was obtained from the device containing 50 wt.% GO loading and was therefore selected for further study.

4.3.3.4 **Evaluation of design parameters on the performance of fMSCs**

To evaluate the influence of \( W \) on device performance, we investigated the devices with different \( W \) (Figure 4.2a) while other parameters such as \( L \) and \( d \) were kept constant (Table 4.2). The film thickness \((T)\) and mass loading of all films were kept at 11.6 \( \mu \)m and 2 mg cm\(^{-2}\), respectively. Increasing \( N \) (\( i.e. \) 4, 8, 12, 20, and 32) corresponded to narrower \( W \) (\( i.e. \) 2400 \( \mu \)m, 1150 \( \mu \)m, 733 \( \mu \)m, 400 \( \mu \)m and 212 \( \mu \)m, respectively). Table 4.2 lists detailed dimensions of all investigated patterns. It can be seen that for similar \( L \) and \( d \), an increasing \( N \) corresponds to a narrowing of \( W \) but this decreases the available active electrode area. The loading of active materials decreased from 95.9% to 73.8% on
each sample when the number of fingers increased from 4 to 32 (based on the same total surface of 1 cm$^2$).

Table 4.2 Dimensions of the fMSC electrodes designed using different width of microelectrode fingers.

<table>
<thead>
<tr>
<th>Name of Device</th>
<th>fMSC (32)</th>
<th>fMSC (20)</th>
<th>fMSC (12)</th>
<th>fMSC (8)</th>
<th>fMSC (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of fingers each device</td>
<td>32</td>
<td>20</td>
<td>12</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Width, W (µm)</td>
<td>212</td>
<td>400</td>
<td>733</td>
<td>1150</td>
<td>2400</td>
</tr>
<tr>
<td>Interspace, d (µm)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Length, L (µm)</td>
<td>8000</td>
<td>8000</td>
<td>8000</td>
<td>8000</td>
<td>8000</td>
</tr>
<tr>
<td>Edge, E (µm)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Area of active materials (cm$^2$)</td>
<td>0.738</td>
<td>0.832</td>
<td>0.869</td>
<td>0.928</td>
<td>0.959</td>
</tr>
<tr>
<td>Total projected area (cm$^2$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4.16 Dependence of the electrochemical properties of the micro-devices on design parameters.
Figure 4.17 Dependence of the electrochemical properties of fMSCs on width of microelectrode fingers. CV curves at (a) 5 mV s\(^{-1}\), (b) 100 mV s\(^{-1}\), (c) 500 mV s\(^{-1}\) and (d) 1000 mV s\(^{-1}\).

The device performance was evaluated using cyclic voltammetry (CV) measurements, which was carried out as a function of scan rate (5 mV s\(^{-1}\) to 2000 mV s\(^{-1}\)) and a voltage window of 1 V (Figure 4.17). At a slow scan rate of 5 mV s\(^{-1}\), all devices exhibited near-perfect rectangular shaped CVs, indicating excellent ion accessibility through the rGO-PEDOT/PSS electrode with only minor ion transport limitation. The capacitance of the whole device (derived from the area of CV curves) increased consistently with the amount of active material in each sample. However, at fast scan rates of 500 and 1000 mV s\(^{-1}\), fMSC(12), fMSC(8) and fMSC(4) samples showed distortion from rectangularity of their CV curves. Only the fMSC(20) and fMSC(32) samples have maintained their rectangular...
CV shape at these fast scan rates, which indicated that fast ion transport was not maintained when $W$ is $>400$ µm. These results also suggested that the fMSC(20) sample is superior among the samples investigated because it has the highest capacitance at fast scan rates (excellent rate capability) and the highest active material loading.

![Figure 4.18](image)

Figure 4.18 (a) Volumetric capacitance, (b) areal capacitance, (c) Ragone plots by volume, and (d) Ragone plots by area of fMSCs with different width of microelectrode fingers.

The observed trend for the scan rate dependence of device capacitance on $W$ was also true for specific capacitance when we normalize the capacitance by volume (Figure 4.18a) and area (Figure 4.18b). For example, at the lowest scan rate of 5 mV s$^{-1}$, the sample with the largest $W$ (fMSC(4)) exhibited the largest volumetric and aerial capacitance (23.0 F cm$^{-3}$ and 26.7 mF cm$^{-2}$, respectively). These values decreased much faster than that of
samples with narrow $W$ when scan rate increased. fMSC(20) exhibited the largest volumetric capacitance among all samples with values of 14.2 F cm$^{-3}$ at 200 mV s$^{-1}$, 12.2 F cm$^{-3}$ at 500 mV s$^{-1}$, 10.0 F cm$^{-3}$ at 1 V s$^{-1}$ and 6.9 F cm$^{-3}$ at 2 V s$^{-1}$. These values surpass that of carbon-based MSCs with sub-micrometer thickness$^{[2,13,26,27,29,30,49,50]}$ and comparable with that of ultrathin-film MSCs$^{[15,20,22]}$ and some pseudo-MSCs$^{[23]}$. The areal capacitance of fMSC(20) at high scan rates was also superior to all samples. The excellent performance of fMSC(20) is also reflected in the energy and power densities (based on the volume or area of the whole device and CV data). fMSC(20) can deliver the highest power density and store comparable energy density compared to other devices (Figure 4.18c and d).

![Nyquist plot of fMSCs with different width of microelectrode fingers.](image)

The device performance was further probed using electrochemical impedance studies. The low frequency part of the impedance spectra of all fMSC samples showed vertical
line that rapidly increased, which is characteristic of capacitive behavior (Figure 4.19).

The high frequency domain (Figure 4.19 inset) showed both small equivalent series resistance (derived from the intercept of the real part of impedance with the x-axis) and charge transport resistance (defined by the size of the semi-circle at high frequency domain) that decreased with $W$. These results further confirm that the decreasing the ionic diffusion path (through the narrowing of $W$) can lower the electrolyte resistance between microelectrodes and thereby increase the ion diffusion rate.

Figure 4.20 Electrochemical performance of fMSC (20). (a) Galvanostatic charge/discharge curves at different current densities (with inset capacitance vs current density). (b) Ragone plot of fMSC (20) and commercially available electrochemical devices.
Further characterization of the fMSC(20) device by galvanostatic charge/discharge (GCD) at various current densities (0.1 mA cm\(^{-2}\) to 2 mA cm\(^{-2}\)) revealed that the slopes of the charge and discharge curves are similar (Figure 4.20a), indicating excellent capacitive characteristic with very high coulombic efficiency (>95 %). The volumetric capacitances calculated from the GCD curves (inset in Figure 4.20b) are consistent with those of the CV curves. There was a minimal iR drop observed at the beginning of the current discharge curve, which indicated low contact resistance in the device.

The fMSC(20) device can also deliver high power and energy densities (4.52 W cm\(^{-3}\) and 3.05 mWh cm\(^{-3}\), respectively). In comparison with some commercialized Li-ion thin film batteries\(^{[2,29]}\) that are presently used in microelectronics, the fMSC(20) device has comparable energy density, but has power density that is more than three orders of magnitude higher (Figure 4.20b). Also shown in this figure is the comparison with commercialized supercapacitors where the fMSC(20) device exhibited significantly higher energy density and comparable power densities. These results demonstrate the exciting potential of these devices for practical applications in energy storage for microelectronics.

The stability of this device was also evaluated by long term charge-discharge measurements (Figure 4.20c). The capacitance retention was 85 % when tested for 10,000 cycles at 1 mA cm\(^{-2}\). After another 10,000 cycles at 2 mA cm\(^{-2}\), the capacitance remained 84 % of the initial capacitance, suggesting that the device has high stability, long cycle life, and high rate capability. This stability can also be reflected from the nearly 100 % coulombic efficiency for all cycles. Electrochemical impedance was also carried out before and after the long-term cycle tests. The equivalent series resistance (ESR) from
the Nyquist plots was only 4.2 Ω (Figure 4.20d), which indicates good electrode conductivity, electrode-current collector contact, and electrolyte conductivity. After these long term cycles, there is only a slight increase in the size of the semi-circle and ESR, suggesting that there is only a small mechanical failure from the polymer doping/dedoping and ion absorbing/desorbing process.\cite{51,52}

4.3.3.5 Increasing the electrode thickness to increase the capacitance of the device.

Electrode thickness is another important parameter that can be used to tune supercapacitor performance.\cite{12,53} In general, device capacitance can be increased by using higher active electrode mass loading, which also results in thicker electrodes.\cite{53} However, an increase in the mass loading and electrode thickness can also increase the electrode resistance and affect the overall device performance (rate capability, aerial and volumetric capacitance).\cite{40,53} Here we investigated the device performance of fMSCs(20) interdigitated device as a function of electrode thickness ($T$, from 6 µm to 58 µm) using CV measurements. These devices were denoted as fMSC(20)-$T$ (e.g. fMSC(20)-6µm for fMSCs with electrode thickness of 6µm).

At a low scan rate of 5 mV s$^{-1}$ (Figure 4.21a), the CV curves of all devices exhibited excellent rectangular shape and a remarkable increase in the area of these curves for devices with thicker electrode was observed. The linear increase in areal capacitance and slight decrease in volumetric capacitance with increasing electrode thickness (Figure 4.22a, solid line) indicate that the electrolyte ions had good access to the interior surface of the active materials at this scan rate. With increasing scan rate, the shape of the CV curves became non-rectangular (Supporting Information Figure S14), as has been
reported for thick electrodes due to the reduced ion diffusion time and longer diffusion path.\cite{53} It is noteworthy that for our devices with thick electrodes (fMSC(20)-58µm), the rectangular shape was maintained at a relatively high scan rate of 200 mV s\(^{-1}\) (Figure 4.21c) indicating that good rate capability was retained.

Figure 4.21 CV curves of fMSC (20) with different electrode thickness.

The areal capacitances of both 84.7 mF cm\(^{-2}\) at 5 mV s\(^{-1}\) and 45.5 mF cm\(^{-2}\) at 200 mV s\(^{-1}\) achieved by the device of fMSC(20)-58µm are significantly higher than the previously reported values for carbon-based MSCs (2.4 – 12.4 mF cm\(^{-2}\)) \cite{13,26,27,30} and MSCs with pseudocapacitive materials (1.2 - 56.3 mF cm\(^{-2}\)) \cite{12,23,24}. Also, slightly decreased volumetric capacitances of 14.5 F cm\(^{-3}\) at 5 mV s\(^{-1}\) and 7.83 F cm\(^{-3}\) at 200 mV s\(^{-1}\) are still comparable with carbon-based MSCs with excellent volumetric capacitive behavior.\cite{2,13,15,20,26,27,29,30,54} In addition, this device delivers an energy density that is
almost four times higher than the fMSC(20)-11µm (13.1 µWh cm\(^{-2}\) vs. 3.46 µWh cm\(^{-2}\), respectively). This excellent device performance, which is much higher than literature reported values, was achieved with only a small decrease in power density (from 8.47 mW cm\(^{-2}\) to 7.51 cm\(^{-2}\), respectively).

Figure 4.22 (a) Areal and volumetric capacitance versus thickness at a scan rate of 5 mV s\(^{-1}\) (solid line) and 200 mV s\(^{-1}\) (dashed line). (b) Ragone plots of fMSCs with different film thickness.

Figure 4.23 (a) Galvanostatic charge/discharge curves of fMSC (20)-58 µm at different current densities (with inset capacitance vs current density). (b) Capacitance retention and coulombic efficiency of fMSC (20)-58 µm during the 10 000 cycles.
The symmetric GCD curves of fMSC (20)-58µm under different current densities signified good capacitive characteristic. The areal capacitances calculated from the GCD curves (inset in Figure 4.23a) are consistent with those of the CV curves. Meanwhile, the capacitance retention of 94.3 % after 10,000 charge/discharge cycles at a current density of 1 mA cm\(^{-2}\) and the excellent coulombic efficiency (close to 100 %) during all 10,000 cycles demonstrate its high cycling stability (Figure 4.23b).

### 4.3.4 Integration of fMSCs

![Single fMSC](image)

![12 fMSCs (6 series × 2 Parallel)](image)

Figure 4.24 Optical images of (a) a green light-emitting diode (LED) powered by single fMSC (20)-58 µm (charged to 1 V), (b) 20 LEDs powered by 12 fMSCs connected in 6 series × 2 parallel (charged to 6 V) on a long strip of flexible rGO-PEDOT/PSS film (1.5 cm × 18 cm).

Due to the low energy stored in limited area, there are few demonstrations of single MSCs as power sources for potential application. In our case, the fMSC(20)-58µm device with high energy density is powerful enough to power a light-emitting diode (LED) (1V) when fully charged (Figure 4.24a). As most of applications require higher voltage window,
tandem fMSCs connected in 6 series × 2 parallel were fabricated from a long strip of flexible rGO-PEDOT/PSS film (1.5 cm × 18 cm). This device was rolled around a wrist to demonstrate its robustness while in operation. Using this configuration, this fMSC device successfully powered 20 small LEDs when fully charged to 6V (Figure 4.24b). These results highlight the exciting potential of these fMSCs in a wide range of applications, especially wearable electronics.

4.4 Conclusion

In Summary, an all-solid-state graphene-PEDOT/PSS-based fMSC have been simply and successfully fabricated through a combination of bar-coating and laser-etching techniques. We demonstrated that the laser-etching is a scalable technique to generate interdigitated electrode patterns due to the simple, quick, and low-cost process. The dimensions and interconnect patterns of these laser-fabricated electrode are easily adjustable to achieve the desired energy, power, current and voltage outputs. In addition, the single fMSC device showed little changes in electrochemical performance when bent at various angles repeatedly for 1,000 times, indicating the robustness required by many practical applications. In the densely-stacked composite electrode, the presence of PEDOT/PSS prevented rGO sheets from re-stacking and improved the electrochemical performance of the assembled fMSCs. After tuning the micro-electrode design (W and T), our all-solid-state fMSC(20) device made from a 58 µm-thick electrode displayed a high areal capacitance (84.7 mF cm⁻² at 5 mV s⁻¹ and 45.5 mF cm⁻² at 200 mV s⁻¹), volumetric capacitance (14.5 F cm⁻³ at 5 mV s⁻¹ and 7.83 F cm⁻³ at 200 mV s⁻¹) and excellent cycling property (>10,000 cycles). The demonstration of powered LED lights using the single and tandem fMSCs highlight the great potential of the scalable fMSCs in real application.
Furthermore, the success of scalable fabrication of tandem fMSCs demonstrates that the Laser-Lithography technology we employ has the potential to make practical advances in device engineering, particularly for device fabrication and design of flexible devices requiring intricate connections, shapes and structures.

4.5 Reference


2013, 25, 2957.


Chapter 5  High Performance Flexible Micro-Supercapacitors by Extrusion Printing of Graphene Oxide/PANi Inks

This chapter is adapted from the article, “Development of Graphene Oxide/Polyaniline Inks for High Performance Flexible Microsupercapacitors via Extrusion Printing” by Yuqing Liu, Binbin Zhang, Qun Xu, Yuyang Hou, Shayan Seyedin, Si Qin, Gordon G. Wallace, Stephen Beirne, Joselito M. Razal, and Jun Chen. This article has been published in Advanced Functional Materials (2018, 1706592). Adapted with permission from Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
5.1 Introduction

Novel and scalable patterning techniques including laser-writing\textsuperscript{[1–3]} and laser-etching\textsuperscript{[4–8]} have been recently applied to large-size film electrode sheets to generate symmetric interdigitated micro-electrode patterns. These techniques are simple, low-cost and allow for facile adjustment of the electrode and device design. However, the fabrication of asymmetric fMSCs for the improvement of the operating voltage window on a single device requires several tedious steps (such as electrodeposition of metal oxides\textsuperscript{[9,10]} and conducting polymers\textsuperscript{[9]}), which can increase the cost on industrial scale fabrication. In addition, the significant volumes of waste materials (\emph{i.e.} etched and unused materials) cannot be avoided in these methods.

Direct printing of active materials is an attractive alternative fabrication method for fMSCs.\textsuperscript{[11–13]} It provides a simple, high speed and scalable approach, and allows fabrication of microelectrodes with a high degree of flexibility in the patterns and geometries. The ability to produce asymmetric fMSCs in a simple way (\emph{i.e.} by changing printing inks) and to control electrode thickness (\emph{i.e.} through the addition of further material layers via additive printing) may also provide some advantages in terms of design flexibility compared to laser based etching techniques. Among various printing techniques, inkjet printing has been widely used to prepare fMSCs. Li \textit{et al.} have shown scalability in fabricating fMSCs by inkjet printing large-scale MSC arrays (12 series \(\times\) 12 parallel) on flexible Kapton\textsuperscript{[14]}. Asymmetric fMSCs based on lamellar (\(\text{K}_2\text{Co}_3(\text{P}_2\text{O}_7)_2\cdot2\text{H}_2\text{O}\)) nanocrystal whiskers and graphene nanosheets were also prepared by printing both the positive and negative electrode materials\textsuperscript{[15]}. However, the processing efficiency is low due to the low solid concentration of inks to ensure compatibility with the inkjet process. Extrusion-based 3D printing, which extrudes viscous ink through a
deposition nozzle is expected to provide higher efficiency.\textsuperscript{[13,16,17]} However, to date there are only a few reports on symmetric fMSCs based on carbon materials (\textit{i.e.} graphene\textsuperscript{[16]} and CNT\textsuperscript{[13]}) and no report on asymmetric fMSCs or fMSCs based on pseudocapacitive materials using extrusion printing techniques. The main obstacle for realizing this technology is the development of appropriate active material ink formulations that meet the extrusion printing processing requirements.

Extrusion printing requires inks with high stability, high viscosity, and homogeneous dispersion of active materials. In recent years, stable suspensions containing capacitive materials (\textit{e.g.} graphene\textsuperscript{[18–21]}, carbon nanotube\textsuperscript{[13]}, polyaniline\textsuperscript{[22–25]}) have been prepared. Strategies to disperse these insoluble materials involve either careful section of organic solvents or the aid of polymer stabilizers or surfactants. However, these suspensions present the following challenges. i) The use of toxic and flammable solvents (\textit{e.g.} dimethylformide, N-methyl-2-pyrrolidone, isopropanol, acetone) needs exhaust and carriage systems and poses safety concerns for mass production of fMSCs. (ii) The electrical conductivity and electroactivity of the materials are affected by the insulating stabilizers or surfactant and post-treatment (\textit{e.g.} high temperature annealing) to eliminate these additives is not compatible with most of the flexible substrates (\textit{i.e.} plastics, papers and textiles). (iii) The concentration of active materials in these inks is usually very low (mostly less than 10 mg mL\textsuperscript{-1} and some less than 1 mg mL\textsuperscript{-1}) and therefore they have low viscosity. Fine and constant lines cannot be formed after low viscosity inks exit nozzle. (iv) Present inks mainly contain a single active nanocarbon (\textit{e.g.} graphene, carbon nanotubes, \textit{etc.}) or pseudocapacitive material (\textit{e.g.} PANi, (K\textsubscript{2}Co\textsubscript{3}(P\textsubscript{2}O\textsubscript{7})\textsubscript{2}\cdot 2H\textsubscript{2}O\textsuperscript{[26]}, Ni(OH)\textsubscript{2}\textsuperscript{[27], etc.}). No ink was developed containing composite materials, which exhibit better performance in lithography-based and laser-etched fMSCs\textsuperscript{[9,28]} (\textit{i.e.} higher
capacitance and rate capability) from robust nanostructures (*e.g.* nano-structured pseudo-materials on carbon templates) and synergistic effects (*i.e.* high conductivity and stability from carbon materials, excellent capacitance from pseudo-capacitive materials).

We build on our previous work (Chapter 4) on aqueous composite formulations of reduced graphene oxide (RGO) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT/PSS) (denoted as RGO-PE) in making viscous inks for extrusion printing. In this work, we made new composite formulations by growing vertically aligned pseudo-capacitive polyaniline (PANi) nanorods on both sides of the graphene oxide (GO) surface. Here, the conductive PEDOT/PSS also functioned as the stabilizer for the GO/PANi composite sheets. By tuning the synthesis conditions and formulation composition, we achieved aqueous-based GO/PANi-PEDOT/PSS (GO/PA-PE) ink with suitable rheology properties for extrusion printing. Upon printing, the microelectrodes can be directly used for the fabrication of fMSCs without any post-processing (*e.g.* no heat treatment needed to remove additives). By repeatedly printing up to 20 layers of GO/PA-PE, the symmetric fMSC device can deliver outstanding device areal capacitance of 153.6 mF cm\(^{-2}\) and volumetric capacitance of 19.2 F cm\(^{-3}\) at 5 mV s\(^{-1}\). We show that it is also possible to fabricate an asymmetric fMSC comprising GO/PA-PE as positive electrode and RGO-PE as negative electrode which demonstrates improvements in voltage window (from 0.8 V to 1.2 V), energy density (from 3.36 mWh cm\(^{-3}\) to 4.83 mWh cm\(^{-3}\)), power density (from 9.82 W cm\(^{-3}\) to 25.3 W cm\(^{-3}\)) and cycling stability (from 75% to 100% capacitance retention over 5000 cycles) compared with the symmetric GO/PA-PE fMSCs.
5.2 Experiment

5.2.1 Preparation of Graphene oxide (GO)/Polyaniline (PANi) hierarchical composite

GO/PANi composite was synthesized by an interfacial polymerization method.[29–31] Typically, GO (~120 mg, prepared by improved Hummers method[32,33]) was dispersed into ~200 mL of 1M H₂SO₄ and the mixture was bath sonicated (Branson B5500R-DTH bath sonicator, 175 W) for 30 min to obtain a well-dispersed suspension. Then APS (~5.70 g) was dissolved in the above solution by further sonicating for 30 min to form the water-phase. Aniline monomers (~2.30 g) were dissolved in ~200 mL of chloroform by bath sonicating for 5 min to form an organic-phase. The organic and water phases were then carefully transferred to a 2 L beaker successively and the reaction was performed at room temperature for ~5 h, during which the initial yellow-brown water-phase gradually changed to dark-green. The resulting product in the water-phase was centrifuged (Eppendorf centrifuge, 4,400 rpm, 10 min) and washed 3 times with ethanol and deionized water by further centrifugation (4,400 rpm, 20 min).

5.2.2 Preparation of printable GO/PANi-PEDOT/PSS Ink

The as-prepared GO/PANi composite, obtained from the above centrifugation, was dispersed in ~100 mL deionized water and bath sonicated for 3 hrs. The concentration of the GO/PANi dispersion was then increased by rotary evaporation. The GO/PA-PE dispersion with various GO/PANi mass loadings from 20 to 80 wt. % were achieved by adding desired amounts of PEDOT/PSS pellets to the above GO/PANi dispersion,
overnight stirring, and bath sonication for 20 mins. The solid content of PEDOT/PSS was maintained at 25 mg mL\(^{-1}\) to form slurry-like ink in all GO/PA-PE ink formulation.

5.2.3 Preparation of printable rGO-PEDOT/PSS Ink

The rGO-PEDOT/PSS dispersion was prepared according to the method we reported previously\(^{[6]}\). The concentration was then increased to \(\sim 20.86\) mg mL\(^{-1}\) by rotary evaporation for the use as an ink for extrusion printing.

5.2.4 Fabrication of fMSCs via extrusion printing

Symmetric and asymmetric fMSCs were produced by directly extrusion printing the as-prepared ink as described in Chapter 2.

5.3 Results and Discussions

5.3.1 Ink Formulations and Printing process

5.3.1.1 Ink stability

Figure 5.1a shows the facile preparation process of aqueous-based GO/PA-PE composite inks. We first vertically attached PANi nano-rods on the GO sheets using an interfacial polymerisation approach and obtained a GO/PANi composite with well-defined nano-structure. We then utilised electroactive PEDOT/PSS as a dispersing agent to achieve highly dispersed water-based GO/PA-PE inks that could meet the stability requirement of extrusion printing. We observed that the GO/PANi composite was not water dispersible (Figure 5.2), although GO sheets have very high dispersibility in water\(^{[22,24]}\).
Scanning electron microscopy (SEM) observations (Figure 5.1b) revealed that the GO sheets were fully covered by water insoluble PANi nano-rods during the polymerization process, which could prevent the access of various hydrophilic functional groups of GO (e.g., hydroxyl and carboxyl). We utilised the high electrostatic interactions of the negatively charged HSO$_3$ groups of PSS with the positively charged anilinium ions of PANi reported previously,[22,34] and attached PEDOT/PSS onto PANi nanorods. SEM studies (Figure 5.1c) showed that the GO surface morphology changed from vertically aligned sharp protrusions to a much smoother surface, which can be explained by the PEDOT/PSS wrapping of PANi nano-rods. The GO/PA-PE (less than 50 wt.% GO/PANi loading) could be dispersed in water, due to the presence of water-dispersible PEDOT/PSS covering the nanostructured GO/PANi composite.

We investigated the effect of GO/PANi weight ratio on dispersibility of GO/PA-PE composites. Precipitations and sediments in the GO/PA-PE dispersion were observed when the GO/PANi loading in the composite was above ~50 wt. % (Figure 5.2). The GO/PA-PE dispersions with less than ~50 wt. % GO/PANi remained homogeneous and sediment-free for more than 1 day, which was sufficient to allow their printing and thus these dispersions were investigated further.
Figure 5.1 (a) Schematic illustration of the preparation of dispersible GO/PA-PE inks. SEM images of (b) GO/PANi and (c) GO/PA-PE composite (50 wt.% GO/PANi).

Figure 5.2 Photo graphs of pure PEDOT/PSS, GO/PA-PE with different GO/PANi loadings, and pure GO/PANi dispersions
Figure 5.3 Optical microscopy images of the following dispersions: PEDOT/PSS, GO/PANi, and GO/PA-PE dispersions with different GO/PANi loadings.

The stability of the dispersions after being settled for one day was also examined by optical microscopy in transmission mode. No obvious particles were observed in the PEDOT/PSS dispersion, indicating its excellent dispersibility in water (Figure 5.3). Small GO/PANi particles were uniformly distributed in GO/PA-PE dispersions with less than ~50 wt. % GO/PANi, while apparent aggregations of large particles were observed in dispersions with above ~50 wt. % GO/PANi loading.
The UV-vis spectra of the aqueous dispersions of all samples confirm the function of PEDOT/PSS as stabilizer (Figure 5.4). In the GO/PANi and all GO/PA-PE samples, two characteristic absorption bands at around 440 nm and 818 nm were observed, which correspond to the polaron-π* and π-polaron transitions in PANi, respectively.\cite{35} While keeping the concentration of GO/PANi the same in all the GO/PA-PE dispersions, these peaks became more distinct with the increased amount of PEDOT/PSS, which indicate that more GO/PANi were distributed uniformly with the assistance of PEDOT/PSS. In addition, the spectrum of GO/PA-PE with 50 wt. % GO/PANi loading was almost unchanged after 1 day, demonstrating the excellent stability of the as-prepared inks.
5.3.1.2 Ink viscosity

We also investigated the rheological properties of GO/PA-PE to identify compositions and formulations that have suitable properties for extrusion printing, *i.e.*, high viscosity and shear thinning behaviour. Having an ink that shows high-viscosity at a low shear rate is necessary for the extrusion printing process because the high viscosity prevents the ink from immediately spreading on the substrate extrusion and thus can form constant lines along the movement direction of the nozzle\(^{[11,13]}\). A good flowability at printing shear rate is also required to make sure the ink can easily flow through the printing nozzles under the applied pressure, thus a shear thinning behaviour of ink is favourable.\(^{[11]}\) We achieved pure PEDOT/PSS dispersions with a concentration up to 25 mg mL\(^{-1}\) that showed a high viscosity of \(\sim 3.9\) Pa\(\cdot\)s at a low shear rate of 1 s\(^{-1}\) (Figure 5.5a), high enough for extrusion printing (0.2 Pa\(\cdot\)s \(\sim 10^4\) Pa\(\cdot\)s at 1 s\(^{-1}\))\(^{[13,36,37]}\) to form fine lines on printing substrates when extruded from moving nozzles. Hence, we maintained the concentration of PEDOT/PSS at 25 mg mL\(^{-1}\) in all GO/PA-PE composite dispersions to achieve reliable printing.

Figure 5.5 (a) viscosity measurement of PEDOT/PSS of different concentrations, and (b) comparison of viscosity between PEDOT/PSS, GO/PA-PE and GO/PANi.
Rheological measurements (Figure 5.5b) showed that the composite ink with the GO/PANi loading of ~50 wt. % had similar shearing thinning behaviour and a slightly higher viscosity (~6.1 Pa•s at 1 s⁻¹) than the pure PEDOT/PSS ink, which was also within the extrusion printing range. The printing shear rate (γ) of the GO/PA-PE ink was calculated to be 833 s⁻¹ from Equation 5.1[38], in which the ink flow rate (Q) was kept at 5 µL min⁻¹ and nozzles with inner radius (R) of 50 µm was used in all printing processes. The low viscosity (0.07 Pa•s) of the GO/PA-PE ink at this shear rate indicates the good flowability of the ink.

\[ \gamma^* = \frac{4Q}{\pi R^3} \]  

Equation 5.1

5.3.1.3 Surface modification on substrates

![Contact angle between GO/PA-PE ink and different substrates.](image)

Figure 5.6 Contact angle between GO/PA-PE ink and different substrates.
The contact angle between ink and substrate needs to be tuned prior to printing. For example, when printing on substrates with poor wettability (contact angle >90°) discontinuous dots form on the substrate, instead of continuous lines; whereas on substrates with a low contact angle, the extruded ink will spread before drying, resulting in poor print resolution. Therefore, we treat the PET and PDMS substrates with oxygen plasma to make them wettable (contact angles of 48.8° and 46.6°, respectively). Glass slides, gold-coated PET and gold-coated PDMS had a contact angle of 69.1° and were therefore used without treatment (Figure 5.6).

5.3.1.4 Printed patterns

Figure 5.7 Digital photos of extrusion printed GO/PA-PE patterns on various substrates.

Figure 5.7 displays the versatility of extrusion printing of various patterns using the GO/PA-PE ink (50 wt. % GO/PANi loading), across a variety of substrates, including polyethylene terephthalate (PET), polydimethylsiloxane (PDMS), and glass. Well-defined patterns including interdigitated electrodes (with different finger widths and distances), spiral and square helix, and electronic circuits could be printed by simply changing the computer-aided design. In our case, the minimum line width of around ~200
µm was printed using a microneedle with an inner diameter of 100 µm (Figure 5.8) and can be expected to be further minimized using smaller diameter needles. The extrusion printed GO/PA-PE lines from an ink with 50 wt. % GO/PA loading had an electrical conductivity of ~64.01 S cm\(^{-1}\) (line width ~ 800 µm and thickness ~ 10 µm), which is comparable with literature reported carbon\(^{[39,40]}\) and conducting polymer\(^{[28,41]}\) electrodes for supercapacitors. Hence, GO/PA-PE lines can be used directly as active materials for fMSCs without post-treatment.

Figure 5.8 Optical microscopy of extrusion printed (a) and (b) interdigitated patterns, (c) and (d) spiral patterns, (e) and (f) the square helix.
5.3.1.5 Ink property and pattern of rGO-PEDOT/PSS

Figure 5.9 (a) Viscosity of RGO-PE dispersion with different concentration and (b) optical microscope images of printed lines.

The viscosity of concentrated RGO-PE ink was also measured (Figure 5.9a). Both the 10 mg mL\(^{-1}\) and 20.86 mg mL\(^{-1}\) dispersion have typical shear thinning behaviour. A great increase in viscosity from 0.05 Pa•s to 30 Pa•s at 1 s\(^{-1}\) shear rate was achieved after concentrating the dispersion from 10 mg mL\(^{-1}\) to 20.86 mg mL\(^{-1}\), which is also in the printable range. The interdigitated microelectrode pattern with similar resolution with the GO/PA-PE patterns can be generated from the concentrated RGO-PE ink (Figure 5.9b).

5.3.2 Physical characterization of GO/PANi-PEDOT/PSS composites

5.3.2.1 Scanning electron microscopy (SEM)

The morphology of extrusion printed GO/PA-PE lines (Figure 5.10) was studied by scanning electron microscopy (SEM). Figure 5.10 a and b show the top-view SEM images of 5-layer printed GO/PA-PE lines, in which all layers were tightly packed to form
seamless printed lines. A very well-defined layer-by-layer structure without any noticeable space between the printed layers was also observed from the cross-sectional SEM images (Figure 5.10c). This observation suggests a very good adhesion between the adjacent printing layers. Some porous structures could be observed between the composite sheets (Figure 5.10d), which is highly desirable in fMSC applications as it is perceived to allow electrolyte penetration and facilitate ion diffusion.

Figure 5.10 (a, b) Top view and (c, d) cross-sectional SEM images of the printed GO/PA-PE pattern.
5.3.2.2  *X-ray diffraction (XRD)*

![XRD pattern of GO, PEDOT/PSS, PANi, GO/PANi, GO/PA-PE samples.](image)

We monitored the structural evolutions at different stages of GO/PA-PE composite preparation using X-ray diffraction (XRD). XRD results showed a downshift in (002) diffraction of the GO from 2θ of ~9.1° in the pure sample to ~7.0° in the GO/PANi composite, which further decreased to ~6.7° on the GO/PA-PE composite (Figure 5.11). Concurrently, the inter-layer *d*-spacing between the GO sheets, calculated from the Bragg’s law\(^{[42]}\) (Equation 2.1), increased from ~0.92 nm (for the pristine GO) to ~1.31 and ~1.37 nm for the GO/PANi and GO/PA-PE, respectively. This gradual increase in
the GO interlayer spacing confirmed our SEM observations (Figure 5.1b and c) that PANi nanorod and PEDOT/PSS wrapped around the GO sheets, which helped the GO sheets remain highly exfoliated and prevented their restacking. In addition, PANi diffractions at $2\theta$ of $\sim18^\circ$ and $\sim26^\circ$ which were present in the GO/PANi composite, became very weak in the GO/PA-PE composite indicating the coverage of PANi nanorods with PEDOT/PSS as observed in SEM studies (Figure 5.1b and c).

5.3.2.3 Raman spectra

The Raman spectra of GO/PANi and GO/PA-PE composites showed the presence of all signature vibrations of PANi emeraldine salt (Figure 5.12). These include the main vibrations in quinoid structure \textit{(i.e.} in plane C-H bending at 1169 cm$^{-1}$, stretching of C-C, C=N, C-N and C-C at 1410, 1474, and 1597 cm$^{-1}$ respectively) and benzenoid rings \textit{(i.e.} amine deformation at 840 cm$^{-1}$ and C-N stretching at 1219 cm$^{-1}$).\textsuperscript{[43,44]} The high intensity of the C-N$^{+•}$ stretching vibration at 1337 cm$^{-1}$ suggested that PANi in the composites was in the doped state.\textsuperscript{[45]} Raman footprints of PEDOT/PSS \textit{(i.e.,} stretching deformation of $C_\beta$-$C_\beta$ at 1372 cm$^{-1}$, $C_\alpha$-$C_\alpha$ inter-ring stretching vibration at 1256 cm$^{-1}$, and oxyethylene ring deformations at 577 and 994 cm$^{-1}$)\textsuperscript{[46]} were all present in the GO/PA-PE composites. However, the D and G bands of the GO\textsuperscript{[47]} were not obvious in the GO/PANi and GO/PA-PE composites. This could be because the GO sheets were totally covered by PANi and PEDOT/PSS which masked the peak of the GO.
Figure 5.12 Raman spectra of GO, PEDOT/PSS, PANi, GO/PANi, GO/PA-PE samples

5.3.2.4 Fourier transform infrared spectra (FTIR)

The FTIR spectra (Figure 5.13) corroborated the Raman results. The PANi related peaks observed in the GO/PANi and GO/PA-PE composites at 1568 cm\(^{-1}\) and 1490 cm\(^{-1}\) (stretching vibration bands of quinonoid and benzenoid rings, respectively), 1290 cm\(^{-1}\) (C-N stretching of secondary aromatic amines), and 1150 cm\(^{-1}\) (C-H of quinonoid ring) indicates the presence of PANi. All the PEDOT/PSS signature peaks at 1167, 1126, 1029 cm\(^{-1}\) (related to S-O and S-phenyl bonds in sulfonic acid respectively) and bands at 1580, 1508, 1001, 894, 771 and 706 cm\(^{-1}\) (corresponding to the C=C, C-C and
C-S bonds in the thiophene backbone respectively) were also observed in the GO/PA-PE composites. The peaks belong to graphene oxide\cite{49} at 1051 cm\(^{-1}\) (alkoxy), 1218 cm\(^{-1}\) (for epoxy), 1409 cm\(^{-1}\) (C-O in carboxy) were surpassed by the peaks of polymers and not visible in the composite samples.

![FT-IR spectra of GO, PEDOT/PSS, PANi, GO/PANi, GO/PA-PE samples](image)

Figure 5.13 FT-IR of GO, PEDOT/PSS, PANi, GO/PANi, GO/PA-PE samples

5.3.3 The role of GO template

The GO component in the composite provides a robust supporting template for the aligned PANi nanorods, and consequently increases the capacitance of PANi. For comparison,
pure PANi was prepared in the absence of GO in the aqueous phase using the same interfacial polymerization method. It is clearly seen in the SEM image that the vertically aligned nanorods are obtained when GO is used (Figure 5.14a), which are also considerably smaller in diameter than the randomly connected thicker PANi nanowires (Figure 5.14b) without the use of GO. This is because the GO template offers abundant nucleation sites for the growth of PANi.\textsuperscript{[50]} The It can be deduced that the PANi component on GO provides an optimized ionic transport pathway and larger ion-accessible surface area, which can enhance the capacitance.\textsuperscript{[50]} To confirm the role of GO in the GO/PA-PE device, fMSCs based on PEDOT/PSS, GO-PEDOT/PSS (GO-PE, 50 wt. % GO loading), PANi-PEDOT/PSS (PA-PE, 50 wt. % PANi loading), and GO/PA-PE (50 wt. % GO/PANi loading) were prepared following the previously used laser-etching method in Chapter 4. The GO-PE and PA-PE formulations were prepared by simply mixing GO and PANi with PEDOT/PSS. The mass loading of the parent film before etching was 2 mg cm\textsuperscript{-2} in all fMSCs. The GO/PA-PE fMSC exhibited highest capacitance and best rate capability performance compared to all other devices (Figure 5.15). Notably, the GO-PE fMSC exhibited lower capacitance than the PEDOT/PSS fMSC. Therefore, the GO component serves as a template for PANi growth with very minimal contribution to the capacitance. In addition, the electrical conductivity of the printed GO/PA-PE lines (width ~ 800 µm and thickness ~ 10 µm) was measured as 64.01 S cm\textsuperscript{-1} which was higher than that of PA-PE (~59.04 S cm\textsuperscript{-1}), and much higher than that GO-PE lines (~6.10 S cm\textsuperscript{-1}), despite the use of insulating GO in the GO/PA-PE composite. This is because of the very small amount of GO in the GO/PANi composite, the polymerization feeding ratio of GO:aniline is 1:19. This ratio ensured that all GO sheets were covered by conductive PANi nanorods and thick PANi nanowires did not grow.
This can also explain why water dispersible GO in GO/PA-PE did not stabilize PANi in water because its functional groups were covered by PANi.

Figure 5.14 Comparison of SEM images between (a) GO/PANi composite and (b) PANi nanowires.

Figure 5.15 Comparison of the electrochemical performance of PEDOT/PSS, GO-PE, GO/PA-PE and PA-PE fMSCs. (a) CV curves at the scan rate of 100 mV s\(^{-1}\), and (b) volumetric capacitance calculated from the CV curves at various scan rates.
5.3.4 Electrochemical characterization of extrusion printed symmetric fMSCs

5.3.4.1 Evaluation of component ratio on the performance of symmetric fMSCs

We fabricated symmetric fMSCs with interdigitated microelectrode patterns (Figure 5.16) and evaluated their electrochemical performance. Briefly, GO/PA-PE composite inks with various GO/PANi loadings (from 20 to 50 wt. %) were extrusion printed on top of pre-patterned interdigitated Au tracks on PET film. Solid-state fMSCs were then assembled using an electrolyte overcoat and electrical connections were established through copper tapes. Table 5.1 and 5.2 list the dimensions of printed patterns and the mass loading of active materials for each fMSC device. Evaluation of all devices revealed that the area of the cyclic voltammetry (CV) curves increased with GO/PA loading at all scan rates (from 5 mV s$^{-1}$ to 500 mV s$^{-1}$, Figure 5.16 b-d). Among all the fMSCs, the device with 50 wt.% GO/PANi loading exhibit the highest volumetric capacitance, and therefore this loading was selected for the next experiments.

Table 5.1 Dimensions of symmetric fMSC patterns

<table>
<thead>
<tr>
<th>Symmetric fMSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of fingers each electrode</td>
</tr>
<tr>
<td>Width, W (μm)</td>
</tr>
<tr>
<td>Interspace, I (μm)</td>
</tr>
<tr>
<td>Length, L (μm)</td>
</tr>
<tr>
<td>Edge, E (μm)</td>
</tr>
<tr>
<td>Area of active materials (cm$^2$)</td>
</tr>
<tr>
<td>Total projected area (cm$^2$)</td>
</tr>
</tbody>
</table>
Table 5.2 Mass loading of active materials and electrode thickness for each device.

<table>
<thead>
<tr>
<th>Name of fMSC</th>
<th>Mass per device (mg)</th>
<th>Mass per area (mg cm⁻²)</th>
<th>Thickness of electrode (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/PA-PE (20 wt% GO/PANi)</td>
<td>0.1175</td>
<td>0.2938</td>
<td>4.5</td>
</tr>
<tr>
<td>GO/PA-PE (33 wt% GO/PANi)</td>
<td>0.1170</td>
<td>0.2925</td>
<td>4.5</td>
</tr>
<tr>
<td>GO/PA-PE (50 wt% GO/PANi)</td>
<td>0.1120</td>
<td>0.2800</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Figure 5.16 (a) Schematic diagram of the fabrication of all-solid-state fMSCs on a flexible PET film using extrusion printing technique. (b) CVs at 5 mV s⁻¹, (c) CVs at 100 mV s⁻¹, (d) CVs at 500 mV s⁻¹. (e) Volumetric capacitance vs. scan rates.
5.3.4.2 GO/PA-PE fMSCs compared with PEDOT/PSS and rGO-PEDOT/PSS fMSCs.

fMSCs from pristine PEDOT/PSS and RGO-PE with 50 wt. % GO loading were also prepared using this method for comparison. The optimal GO/PA-PE (with 50 wt.% GO/PANi loading) fMSC showed superior performance over the neat PEDOT/PSS and RGO-PE fMSC in terms of capacitance, charge transfer rate, energy and power densities (Figure 5.17). It is noteworthy that PEDOT/PSS serves as a conductive and flexible dispersant to facilitate ink preparation and the printing process and only contributes a small amount of capacitance (i.e. 3.32 F cm$^{-3}$ at 5 mV s$^{-1}$). Most of the capacitance in the composite fMSCs comes from the active materials (i.e., rGO and the well-ordered PANi on GO template, respectively). The GO/PA-PE fMSC device exhibited two pronounced redox responses for PANi (i.e., the leucoemeraldine/emeraldine and emeraldine/pernigraniline structural transitions), making the capacitance higher than the RGO-PE fMSC device. Meanwhile, the larger capacitance and the quasi-square shape of the CV curves at all scan rates of 5-500 mV s$^{-1}$ (Figure 5.17a-e) further demonstrate GO/PA-PE fMSC’s fast charge transfer rate and excellent rate capability. The excellent performance of GO/PA-PE fMSC is also reflected in the energy and power densities (Figure 5.17f, calculated from the CV data based on the volume of the whole device). The GO/PA-PE fMSC showed an energy density and a power density of ~3.36 mWh cm$^{-3}$ and ~9.82 W cm$^{-3}$ respectively, which were found to be higher than the RGO-PE (~1.03 mWh cm$^{-3}$ and ~4.84 W cm$^{-3}$, respectively) and PEDOT/PSS fMSCs (~0.33 mWh cm$^{-3}$ and ~5.3 W cm$^{-3}$, respectively).
Figure 5.17 Performance comparison of PEDOT/PSS, RGO-PE, GO/PA-PE devices (a) CVs at 5 mV s$^{-1}$, (b) CVs at 50 mV s$^{-1}$, (c) CVs at 100 mV s$^{-1}$, (d) CVs at 500 mV s$^{-1}$ (e) volumetric capacitance vs scan rate, (f) energy and power densities.

The GO/PA-PE fMSC device showed an excellent volumetric capacitance of ~37.8 F cm$^{-3}$ (areal capacitance ~17.5 mF cm$^{-2}$) at the scan rate of 5 mV s$^{-1}$ which was maintained ~80% and ~66% at the high scan rate of 100 mV s$^{-1}$ and 500 mV s$^{-1}$, respectively. The volumetric and areal capacitances of the GO/PA-PE fMSC device exceeds those of
carbon-based fMSCs\textsuperscript{[2-5,51,52]} and are comparable with those of pseudocapacitive material-based fMSCs with sub-micrometer thickness \textsuperscript{[9,48,53-55]}, although less than 50 wt.\% PANi was used in composite electrodes. It is noteworthy that the areal capacitance is relatively low when compared with thicker pseudocapacitive fMSCs (with electrode thickness > 10 µm). That is due to the GO/PA-PE fMSC being made from only 2-layer extrusion printed microelectrodes with low electrode thickness of 4.6 µm and active materials mass loading of 0.28 mg cm\textsuperscript{-2}. Hence, the areal capacitance is expected to be further increased with increased electrode thickness.

![Graphs showing GCD curves](image)

Figure 5.18 Comparison of the GCD curves of the GO/PA-PE fMSC with PEDOT/PSS and RGO-PE fMSCs at the current density of (a) 0.1 mA cm\textsuperscript{-2}, (b) 0.5 mA cm\textsuperscript{-2}, (c) 1 mA cm\textsuperscript{-2}. (d) Volumetric capacitance of the fMSCs calculated at different current densities.
The GCD curves of GO/PA-PE fMSC clearly showed longer discharge time than the pure PEDOT/PSS and RGO-PE fMSCs at all constant discharge currents, indicating its higher capacitance and its excellent rate capability (Figure 5.18). The symmetric charge-discharge curves and minimal iR drop at the beginning of the constant current discharge suggest good capacitive behavior and low contact resistance of the GO/PA-PE fMSC device. This result is in consistence with the CV results.

Figure 5.19 Nyquist plots for PEDOT/PSS, RGO-PE, and GO/PA-PE fMSCs.

The small charge transport resistance ($R_{ct}$, derived from the radius of the semi-circle at high frequency region) and the high slop of the vertical line in the low frequency region of the Nyquist plots (Figure 5.19) suggest fast ion-diffusion rate and good capacitive behavior for the GO/PA-PE fMSC, although the GO/PA-PE fMSC exhibits larger equivalent series resistance (ESR, defined by the intercept of the real part of impedance with the x-axis) than the RGO-PE and PEDOT/PSS device.
Evaluation of printed layers on the performance of symmetric fMSCs

Extrusion printing is a simple technique to increase the interdigitated electrode thickness by repetitive layer-by-layer printing of electrode materials. The volume of extruded inks was kept the same per layer, so the mass loading of active materials increased linearly (from 0.28 mg cm$^{-2}$ to 2.8 mg cm$^{-2}$) to the number of printing layers (from 2 to 20 layers). Accordingly, the electrode thickness increased from 4.6 µm to 80 µm without expanding the finger electrode width (Figure 5.20 and Figure 5.21). The thickness of the electrode did not linearly increase with printing layers because the top layers of electrode finger became narrower and thicker than the bottom layers (Figure 5.21). Upon exiting the printing nozzle, the printed ink lines not only spread laterally as they do on solid and smooth Au-PET substrate, but they also spread downwards into the porous bottom (previous) layer of the electrode materials. Therefore, the thicker the undried underneath layer, the less link will spread along the lateral direction, resulting in narrowing the line width and increasing the line thickness.
Figure 5.20 (a) Illustration of thickness measurements via Dektak profilometer, (b) thickness profile of fMSCs with different printed layers. (c) thickness and mass loading of electrode materials in fMSCs with printing layers.

Figure 5.21 (a) Cross-sectional SEM images and (b) thickness profile of a 20-layer printed electrode finger.
Figure 5.22 Electrochemical performance of fMSCs with different printed layers. (a) CV curves at 5 mV s\(^{-1}\), (b) CV curves at 100 mV s\(^{-1}\) (c) CV curves at 200 mV s\(^{-1}\), (d) CV curves at 500 mV s\(^{-1}\), (e) areal and volumetric capacitance of fMSCs with printing layers, and (f) Ragone plot.

We evaluated the effect of printed layers on the areal device performance using CV measurements at different scan rates (Figure 5.22a-d). We observed that at the low scan
rate of 5 mV s\(^{-1}\), the area of the CV curve increased with the number of printed layers and all devices exhibited rectangular CV shape with the two pronounced redox peaks of PANi (Figure 5.22a). The analysis of CV results at this scan rate showed that the areal capacitance of the fMSC device increased linearly from 17.5 to 153.6 mF cm\(^{-2}\) with increasing number of layers from 2 to 20 (Figure 5.22e, solid line). This increase in the areal capacitance indicates that the electrolyte ions had good access to the interior surface of the active materials. When the scan rate increased from 5 to 500 mV s\(^{-1}\), the shape of the CV curve became slightly distorted and the redox peaks gradually weakened (Figure 5.22a-d). These observations can be attributed to the shorter ion diffusion time at high scan rates, and increased electron transfer and ion diffusion path. It is notable that at 100 mV s\(^{-1}\) the CV curve of the 20-layer device maintained its CV response (i.e., square shape and apparent redox peaks), indicating that good rate capability (Figure 5.22b).

The areal capacitance of 153.6 mF cm\(^{-2}\) at 5 mV s\(^{-1}\) and 98.9 mF cm\(^{-2}\) at 100 mV s\(^{-1}\) achieved on the 20-layer device are significantly higher than all fMSCs based on carbon\(^{[2-5,51,52]}\) and pseudocapacitive materials\(^{[9,28,53-57]}\). The slightly decreased volumetric capacitances of 19.2 F cm\(^{-3}\) at 5 mV s\(^{-1}\) and 12.4 F cm\(^{-3}\) at 100 mV s\(^{-1}\) are also comparable with most of the carbon-based and pseudo-capacitive fMSCs (Table S3). It is generally shown that volumetric capacitance decreases greatly with thickness and areal capacitance can reach a plateau when thickness reaches the micro-meter range, due to the increased electrode resistance and the reduced electrolyte penetration and ion transfer for thick and dense electrode.\(^{[28]}\) The constant increase in areal capacitance with thickness of the GO/PA-PE fMSCs is partly attributed to the porous hierarchical structure of the electrode materials. The other reason is the presence of the highly conductive and ion permeable PEDOT/PSS, which not only serves as a dispersing agent, but also facilitates the
penetration and transfer of electrolyte ions in between the inner surface of electrode materials. It is notable that this 20-layer device also delivered an excellent areal energy density that is nearly 10 times higher than the 2-layer fMSC (15.4 $\mu$Wh cm$^{-2}$ vs. 1.7 $\mu$Wh cm$^{-2}$, calculated from the CV data) without sacrificing the power density (increased from 4.55 mW cm$^{-2}$ to 6.34 mW cm$^{-2}$), which is higher than most pseudo-capacitive fMSCs$^{[9,28,53-57]}$ (Figure 5.22f). Despite that the 20-layer fMSC undergoing a decrease in volumetric energy density (from 3.36 mW cm$^{-3}$ to 1.93 mW cm$^{-3}$) and power density (from 9.82 W cm$^{-3}$ to 0.793 W cm$^{-3}$) compared with the 2-layer fMSC, the values are still comparable with literature reported thick fMSCs$^{[3,9]}$ (electrode thickness > 10 $\mu$m).

The symmetric GCD curves suggest good capacitive characteristics of all devices at different current densities (Figure 5.23). The increasing discharge times with printing layers indicate an increase in capacitance, which is consistent with the CV results.
Figure 5.23 GCD curves of GO/PA-PE fMSCs with different printing layers at various current densities of (a) 0.1 mA cm$^{-2}$, (b) 0.5 mA cm$^{-2}$, and (c) 1 mA cm$^{-2}$.(d) calculated capacitance versus current densities.

Figure 5.24 Nyquist plots of fMSCs with different printing layers.

The Nyquist plot of fMSCs with different printed layers, showed high slope for the low-frequency region and small $R_{ct}$ in the high frequency part region for all devices, indicating their excellent capacitive behaviours (Figure 5.24). ESR also decreased from 21.3 $\Omega$ to 7.89 $\Omega$ when printing layers increased from 2 to 20. These observations are different in contrast with the previous reports on supercapacitors with sandwiched design$^{[58]}$, where the low-frequency slope decreased, and $R_{ct}$ and ESR increased sharply with electrode thickness. This is because in interdigitated design, the electrolyte ions could penetrate and diffuse along the parallel direction of the layered electrode materials as opposed to being limited to just the vertical direction in the conventional sandwiched design. Consequently, the ion accessible surface of electrode materials and ion transport length are not affected by the electrode thickness in interdigitated design. Meanwhile, the electron can also
transport along the parallel direction in interdigitated design, hence the ESR becomes smaller for the thicker electrode due to the larger cross-section area (A) of the electrode (according to \( R = \rho l / A \), where \( R \) is electrical resistance, \( \rho \) is electrical resistivity, and \( l \) is the length of the electrode).

### 5.3.4.4 Compared with sandwiched structured fMSCs.

Table 5.3 Detailed comparison of the dimensions of sandwiched and interdigitated fMSCs.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sandwiched fMSC</th>
<th>Interdigitated fMSC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Device parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active materials loading of device</td>
<td>2.8 mg cm(^{-2})</td>
<td>2.8 mg cm(^{-2})</td>
</tr>
<tr>
<td>Mass of active materials</td>
<td>1.12 mg</td>
<td>1.12 mg</td>
</tr>
<tr>
<td>Size of device</td>
<td>0.8 cm × 0.5 cm</td>
<td>0.8 cm × 0.5 cm</td>
</tr>
<tr>
<td>Device thickness</td>
<td>112 µm</td>
<td>80.2 µm</td>
</tr>
<tr>
<td><strong>Each electrode parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrode mass</td>
<td>0.56 mg</td>
<td>0.56 mg</td>
</tr>
<tr>
<td>Electrode thickness</td>
<td>9.48 µm</td>
<td>80 µm</td>
</tr>
<tr>
<td>Electrode footprint area</td>
<td>0.4 cm(^{2})</td>
<td>0.14 cm(^{2})</td>
</tr>
</tbody>
</table>

The interdigitated design also enhanced the overall device performance (in both capacitance and rate capability), as the electrolyte ion can penetrate and diffuse along the parallel direction of the layered electrode materials in the interdigitated design as opposed to being limited to just the vertical direction in the conventional sandwiched design.\([40,47,59]\)

Therefore, the ion accessibility of electrode materials and ion diffusion pathway will not be greatly affected in devices with thick electrodes. For comparison, we fabricated a
supercapacitor device with the conventional sandwiched design by facing two GO/PA-PE films (with mass loading of 1.4 mg cm\(^{-2}\) per film) to each other and adding a layer of PVA/H\(_3\)PO\(_4\) gel electrolyte in between. The performance of the sandwiched-fMSC was compared with the 20-layer interdigitated-fMSC device that had the same total active material mass loading of 2.8 mg cm\(^{-2}\) (see detailed parameter and device dimensions in Table 5.3). The interdigitated-fMSC showed a larger area in the CV curves than the sandwiched-fMSC device (Figure 5.25). The areal and volumetric capacitance of the interdigitated fMSC device at 2 mV s\(^{-1}\) was ~170 mF cm\(^{-2}\) and 21.7 F cm\(^{-3}\), which was higher than that of the sandwiched-fMSC (~100 mF cm\(^{-2}\) and 9.71 F cm\(^{-3}\)).

Figure 5.25 Performance comparison between fMSCs with sandwiched and interdigitated designs. (a) CV curves at 50 mV s\(^{-1}\), (b) areal capacitance, and (c) volumetric capacitance.

5.3.5 Electrochemical characterization of asymmetric fMSCs.

5.3.5.1 Design parameters of asymmetric fMSCs.

The device performance was further improved by making asymmetric fMSCs (AfMSCs). The fabrication of this device is practicable via extrusion printing, in which the positive (GO/PA-PE) and the negative (RGO-PE) electrodes were separately printed using two print-heads. Prior to printing, the charge balance between the two electrodes (\(i.e. q_+ = q_-\))
was carefully regulated to keep the stable operation of AfMSCs. Hence, the RGO-PE and GO/PA-PE electrodes were first characterized to identify the stable potential range and specific capacitance (Figure 5.26). On the basis of the Equation 5.2 and 5.3 (m is the mass of active materials, C is the gravimetric capacitance and ΔE is the stable voltage window, the subscript of + and – represents the positive and negative materials respectively), the optimal mass ratio between the two electrodes should be \( m_+/m_- = 0.52 \).

\[
q = C \times m \times \Delta E \quad \text{Equation 5.2}
\]

\[
\frac{m_+}{m_-} = \frac{C_+ \Delta E_-}{C_- \Delta E_+} \quad \text{Equation 5.3}
\]

It is obvious that the mass difference would inevitably cause volume differences of the two electrodes, which can be achieved by varying either electrode thickness (named as AfMSC-T) or the electrode foot-print area (AfMSC-A). The former method was
employed in most supercapacitors including sandwiched and interdigitated design. It is reasonable in sandwiched supercapacitors where the two film electrodes that face each other possess the same area. However, in supercapacitors with interdigitated electrodes, there would be space waste above the thin electrodes. In this case, the volume of the total device would be increased, which is not desirable considering fMSCs applications in microelectronics. Hence, we are trying to propose a better design which achieves the weight ratio balance via varying the footprint area and keeping the electrode thickness consistent.

The mass density of the two materials was measured to be \(~1.46 \text{ g cm}^{-3}\) and \(~1.40 \text{ g cm}^{-3}\) for GO/PA-PE and RGO-PE film respectively. Based on Equation 5.4 (\(A, T, V, \text{ and } D\) is the footprint area, thickness, volume and mass density of active materials, respectively, the subscript of + and – represents the positive and negative materials respectively), the area ratio was calculated to be \(A_+ / A_- = 2.01 \approx 2\), which would be realized by varying the width of interdigitated fingers (AfMSC-A, Figure 5.27a-c) during printing. The thickness of extrusion printed asymmetric interdigitated microelectrodes was measured to be constant at 3.6 \(\mu\)m and the device was named as AfMSC-A. Another asymmetric device (AfMSC-T) with device thickness of 6 \(\mu\)m which utilizes the traditional design (i.e., keeping area the same while varying electrode thickness) was also printed for comparison. With the same active materials mass loading, the two devices exhibit similar CV curves, indicating the same device capacitance (Figure 5.28a). However, when comparing the volumetric capacitance, device AfMSC-A is larger than device AfMSC-T, showing the superior performance originated from the optimized space arrangement of electrodes (Figure 5.28b). Therefore, AfMSC-A device was therefore selected for further investigation.
\[
\frac{A_+}{A_-} = \frac{V_+}{V_-} = \frac{V_+}{V_-} = \frac{m_+}{m_-} = \frac{D_+}{D_-} \quad \text{Equation 5.4}
\]

Figure 5.27 Illustration and dimensions of AfMSC-T and AfMSC-A.

Figure 5.28 Performance comparison between AfMSC-A and AfMSC-T.
5.3.5.2 Electrochemical performance of optimized asymmetric fMSCs.

Figure 5.29b shows the CV curves of the as-fabricated AfMSCs-A device with different operating voltage windows varying from 0-0.8 to 0-1.2 V at a scan rate of 50 mV s⁻¹. The square shape and obvious redox peaks were observed in all curves, indicating that the voltage window can be increased from 0.8 V to 1.2 V in asymmetric fMSCs. It is notable that these features of CV curves were retained even at a very high scan rate of 1000 mV s⁻¹ (Figure 5.29c). For the GO/PA-PE symmetric fMSCs these features could only be maintained at 500 mV s⁻¹ (Figure 5.16). The enhancement in rate capability can be attributed to the better electrical conductivity of RGO-PE (82.8 S cm⁻¹) than GO/PA-PE (64.01 S cm⁻¹). The symmetric GCD curves and the calculated steady capacitance at all current densities (0.05 - 2 mA cm⁻²) also demonstrate the excellent AfMSC device performance, e.g. capacitive behaviour and rate capability (Figure 5.30).
Figure 5.29 (a) Schematic illustration and digital photograph of extrusion printed AfMSC. (b) CV curves of AfMSCs measured at different potential window at a scan rate of 50 mV s⁻¹. (c) CV curves of AfMSCs at different scan rates (from 100 mV s⁻¹ to 1000 mV s⁻¹) with a voltage window of 1.2 V. (d) Ragone plots comparison of GO/PA-PE symmetric fMSCs and AfMSCs. The data for Li-ion thin film battery and commercial supercapacitor are reproduced from ref. [4] (e) Capacitance retention of the symmetric and asymmetric fMSCs during the 10 000 cycles.
Figure 5.30 (a) GCD curves and (b) volumetric capacitance of the AfMSC measured from the GCD curves at different current densities.

The performance of AfMSCs was also compared with symmetric fMSCs (SfMSC, using GO/PA-PE electrodes) of similar mass loading of total active materials. The capacitance of the AfMSC (25 F cm$^{-3}$ at 5 mV s$^{-1}$) is relatively lower than that of SfMSC (37.8 F cm$^{-3}$ at 5 mV s$^{-1}$). However, the higher energy density (from 3.36 mWh cm$^{-3}$ to 4.83 mWh cm$^{-3}$) and power density (from 9.4 W cm$^{-3}$ to 25.3 W cm$^{-3}$) of AfMSC in comparison to the symmetric fMSC illustrates the merits of the increased voltage window in AfMSC. This energy density is comparable to some commercial Li-ion thin film batteries but has a power density more than three orders of magnitude higher (Figure 5.29d). The device also delivers significantly higher energy density and comparable power densities compared with commercial 3.5V / 25 mF supercapacitors. These values are also higher than some AfMSCs such as LIG-FeOOH//LIG-MnO$_2$)$^{[9]}$, (K$_2$Co$_3$(P$_2$O$_7$)$_2$ • 2H$_2$O//graphene$^{[26]}$, and most of the carbon-based symmetric fMSCs$^{[1-3,51,59-61]}$ and some fMSCs based on pseudocapacitive materials$^{[9,53-56]}$. Furthermore, the AfMSCs have better capacitance retention after long term cycling than the symmetric fMSCs (Figure 5.29e). Similar to other literature reports$^{[9,32,58,62]}$, some small fluctuations in capacitance were
observed in the charge/discharge cycles when the applied current density became relatively high (690 mA cm$^{-3}$ for asymmetric and 550 mA cm$^{-3}$ for symmetric fMSCs). However, after 5,000 consecutive cycles the capacitance retention of AfMSCs was almost 100% of its initial capacitance (charged up to 1.2 V), while the symmetric fMSCs only retained 70% of the initial capacitance (charged to 0.8 V). The values dropped to 96% and 65% respectively after 10,000 cycles. The instability of GO/PA-PE symmetric fMSC originates from the high current densities used in this study. At high current densities, PANi encounters fast redox reactions and rapid volume expansion during the charge/discharge process, which leaves PANi insufficient recovery time during each cycle. The excellent long cycle life of AfMSCs is due to the appropriate charge balance between the positive and negative electrodes, and the good electrochemical stability of the RGO-PE electrodes.

![Nyquist plot](image)

Figure 5.31 Nyquist plot of symmetric and asymmetric fMSCs.
The improvement in rate capability of asymmetric fMSC can also be explained by the impedance analysis of the Nyquist plot. In Figure 5.31, the asymmetric fMSC shows small ESR and $R_{ct}$ in the high frequency region and a vertical slope in the low frequency region, which are the characteristics of the good capacitive behaviour and fast ion-transport rate. Specifically, the ESR of the asymmetric fMSC (14 Ω) is smaller than that of GO/PA-PE symmetric fMSC (21 Ω) due to the use of more conductive RGO-PE in the asymmetric fMSCs. The slightly larger $R_{ct}$ of the asymmetric device as displayed by the small semi-circle in the high-frequency part and the small reduction in slope in the low-frequency region can be explained by the increase in electrode finger width where the ion-transport between electrodes becomes longer.

5.3.6 Flexibility and durability of fMSCs.

Figure 5.32 (a) Photograph of the AfMSC device at the bent state. (b) Comparison of the CV curve of the device before and after bending at different conditions. Also shown is the CV curve after repeated bending of the AfMSC device at 150 ° for 1000 times. Testing was performed at the scan rate of 100 mV s$^{-1}$. 
The performance of the device was also tested under various bending conditions. There is negligible change in the CV curves when the device was bent at various degrees (60 ° to 150 °) or was subject to repeatedly bending at 150 ° for 1000 times (Figure 5.32), indicating the excellent endurance to bending even during device operation.

5.3.7 Connection between multi fMSCs

Figure 5.33 (a-c) photos of four connected fMSCs on PET film. (a) in series, (b) in parallel, (c) in a combination of series and parallel, and (d-f) CVs profiles at the scan rate of 100 mV s⁻¹. GCD curves (current density = 0.25 mA cm⁻²) of four fMSC devices connected in (g) series, (h) parallel, and (i) combination of series and parallel.

Multiple capacitors can be connected together in series or parallel configurations in many applications to meet the current or voltage requirement which cannot be delivered by a single supercapacitor device. However, the electrical connections between fMSCs and
the electrochemical isolation between single devices (i.e., electrolyte isolation) often involve additional fabrication steps (e.g., electrically connecting via conducting wires and making isolation mask using kapton tape). Our extrusion printing technique provides a facile solution for these issues. As shown in Figure 5.33, the extrusion printer can print both the interdigitated electrodes and the necessary connections between devices. The PDMS cell barriers were also extrusion printed, and acts to repel the wet polymer gel electrolyte and enable electrochemical isolation of fMSCs that are close to each other. Figure 5.33 shows the performance of the small-scale connection of four AfMSCs in series, parallel and the combination of these two configurations. A wide voltage window of 4.8 V can be achieved by the four AfMSCs connected in series (Figure 5.33d), and the output current of the parallel configuration also increased by four times compared with the single AfMSC (Figure 5.33e). The combination of two series and two parallel connections increased the voltage window to 2.4 V without decreasing the output current, suggesting excellent connection between individual devices (Figure 5.33f). The GCD curves (Figure 5.33g-i) also show that it is possible to enhance the output voltage and discharge time by connecting several devices in series and parallel respectively. These results suggest the excellent connection between individual devices.

5.4 Conclusion

In conclusion, we have developed extrusion printable GO/PANi and graphene inks with the assistance of the PEDOT/PSS stabilizer. The use of PEDOT/PSS has not only improved the materials’ (i.e., GO/PANi and graphene) printability in terms of water stability and viscosity, but also endows the materials with high electrical conductivity and enables full utilization of inner surface capacitance. The extrusion printed GO/PA-PE
based symmetric fMSCs exhibit higher areal capacitance (153.6 mF cm\(^{-2}\) at 5 mV s\(^{-1}\), 99 mF cm\(^{-2}\) at 100 mV s\(^{-1}\)) and comparable volumetric capacitance (19.2 F cm\(^{-3}\) at 5 mV s\(^{-1}\), 12.4 F cm\(^{-3}\) at 100 mV s\(^{-1}\)) than literature reported values. In addition, the AfMSC showed 100% capacitance retention over 5000 cycles due to the appropriate charge balance between the two electrodes. The extrusion printed asymmetric fMSCs with GO/PANi-PEDOT/PSS and graphene-PEDOT/PSS as positive and negative materials, respectively, possess a widened voltage window (1.2 V) and an improved energy density (4.83 mWh cm\(^{-3}\)), power density (25.3 W cm\(^{-3}\)). Furthermore, extrusion printing enables the feasible construction of several connected fMSCs on a substrate, which makes it practical in real applications that require higher current or voltage. Both the simple ink preparation process and facile device fabrication technique are highly scalable. The extrusion printed high-performance fMSCs are especially promising for integration for use as a power source that can be directly integrated into the next-generation of printed wearable microelectronics.

5.5 Reference


Chapter 6  Conclusion and Perspectives
6.1 General conclusions

To conclude, this thesis has been focused on the facile fabrication of film and interdigitated electrodes for flexible supercapacitors, which have potential in the use of wearable electronics. Optimization was made in terms of flexible electrode materials, device architecture design, suitable technologies to achieve advanced device performance step-by-step (Figure 6.1). Specifically, the work started with the simple preparation of large-size and flexible rGO-PEDOT/PSS composite film via bar-coating method. In the
film, PEDOT/PSS was utilized as flexible and conductive matrix, and at the same time, preventing the re-stacking problem of rGO. The film has high electrical conductivity and good electrolyte ion accessibility to the inner surface of electrode materials, which enables high areal capacitance of 448 mF cm\(^{-2}\) when the film with high mass loading of 8.49 mg cm\(^{-2}\) was used in the flexible all-solid-state SCs with sandwiched structure. Then a simple laser-etching process was applied on the large-size rGO-PEDOT/PSS film to generate interdigitated micro-electrodes for flexible micro-supercapacitors (fMSCs). The fMSCs with interdigitated design has greatly improved the volumetric capacitance from 3.15 F cm\(^{-3}\) to 19.2 F cm\(^{-3}\), compared to that with sandwiched design. Meanwhile, the easy series and/or parallel design on the same substrate made it practical in the use of wearable microelectronics. The performance of fMSCs was further improved via incorporating the pseudo-capacitive materials of PANi (to increase capacitance) and employing an asymmetric design of the device (to widen voltage window). Another scalable and simple patterning technique of extrusion printing was employed to achieve this goal. Great improvement in energy and power density of 4.83 mWh cm\(^{-3}\) and 25.3 W cm\(^{-3}\) were achieved by the extrusion printed GO/PANi-PEDOT/PSS || rGO-PEDOT/PSS asymmetric fMSCs, compared to the laser-etched rGO-PEDOT/PSS fMSC in Chapter 4 (3.05 mWh cm\(^{-3}\) and 4.52 W cm\(^{-3}\)).

It is notable that all the electrode fabrication techniques utilized in this work including bar-coating, laser-etching and extrusion printing are simple, cost-effective and practical for large-scale production and all the fabricated devices can achieve comparable areal and volumetric capacitance with literature reported high values. Therefore, we anticipate the devices fabricated in this work has great potential in the real application of wearable electric systems.
6.2 Perspectives

Despite of the facile and practical strategies in scalable fabrication of high-performance flexible supercapacitors provided in this thesis, further improvements are still required in both materials and engineering aspects to achieve industry-level performance and promote manufacture process.

Figure 6.2 (a) Potential novel pseudo-capacitive materials to be incorporated into the Rgo-PEDOT/PSS system. (b) Illustration of different pattern designs of fMSCs. (c) Different designs in developing 3D structured fMSCs. (d) Integration examples of fSCs and fMSCs. Reproduced from ref. [1–6] with permissions from Wiley publishing group and the Royal Society of Chemistry.

The established layer-by-layer graphene-PEDOT/PSS system in this work has enabled the easy fabrication of high performance electrodes with high areal mass loading and thickness, which reaches the commercial standard of electrode loading (mass loading at
least 5 mg cm\(^{-2}\) and thickness range between 50 ~ 200 µm) in real application. The incorporation of pseudo-capacitive PANi has greatly increased the capacitance and energy density while maintaining the similar loading level of electrode materials. Utilizing the merits of PEDOT/PSS in film processing (i.e. excellent water-dispersibility and flexible film forming property), other layer-by-layer film electrodes like MoS\(_2\)-PEDOT/PSS\(^7\) and Mxene-PEDOT/PSS\(^8\) were developed recently. Pseudocapacitive materials with high theoretically high capacitance, including Ppy, metal oxides (such as MnO\(_2\)), and new generation of advanced materials (like cobalt-nickel sulphide (NiCo\(_2\)S\(_4\))\(^1\), metal organic-frameworks (MOFs)\(^2\), Mxene\(^9\) etc), are also expected to be added into these layer-by-layer system to pursue better electrochemical performance (Figure 6.2a). Facile synthesis and incorporation methods of these materials need to be developed and modified to achieve the desired nanostructures and device performance.

The designs of interdigitated electrodes with three-dimensional structures are also expected to be developed. Different pattern designs (e.g. interdigitated, and spiral patterns\(^3\)) and pattern parameters (detailed size of microelectrodes) in the planar direction can be studied to achieve optimized performance (Figure 6.2b). It is reported that layer-by-layer assembled electrodes with different materials on each layers exhibit superior performance than electrodes with randomly mixed materials\(^{10,11}\). This design is technically practical by printing several layers of materials separately but needs further investigation.

Direct printing of active materials is simple, low-cost, and time-saving manufacturing technology for flexible supercapacitor fabrication, which has good perspective for industry-level manufacture. To date, suitable inks were only investigated from a limited
number of active materials (like graphene and CNT), more efforts can be paid to designing various nanomaterials-based ink formulations. As most active materials are not solvent processable, additives which can meet the rheological requirements without affecting the nanostructure, electrical conductivity and sacrificing the electrochemical performances should be developed. In addition, the post-treatment to remove additives is expected to be waived or should be technically compatible with the flexible substrates which are normally plastics. Moreover, fast-drying and environmental friendly solvent is preferred to ease the burden of safety, exhaust and carriage systems for mass production.

Fully printed fSC devices are also promising to be developed via printing on condition that current collectors, electrolyte and packaging materials are printable. Ink-jet\textsuperscript{[4]}, screen\textsuperscript{[12]}, and gravure printable\textsuperscript{[13]} silver suspensions or pastes have been used to fabricate interdigitated patterned current collectors. Efforts are being paid to developing ink-jet printable electrolytes\textsuperscript{[4]}, which can be printed precisely on top of each small size fSCs and enabled electrochemical isolation of fSCs that were positioned close to each other (Figure 6.2c). In addition, the polydimethylsiloxane (PDMS), which is widely used to pack and seal fSCs, is extrusion printable. We believe that the fully printing of a series of connected fSCs devices can be achieved to simplify the fabrication steps in mass production. However, to realize this aim, further efforts should be paid to develop printable inks of every component (including electrode materials, current collector, and electrolyte) in a facile and cost-effective method.

The integration of flexible supercapacitors to the new generation wearable electronic system (including the flexible units of energy harvesting and electronic devices) has attracted much attention. A fabric based fSCs, together with tribo-electric generators and
pressure sensor, was sewn into knitted shirts and connected by conductive threads to store charges generated from human activities and provide power for pressure sensors.\cite{5}

Integration to textile and clothes is a trend for fSCs with sandwiched structure in wearable application. In recent years, research on body-attached sensing devices, which are fabricated on a stretchable, bio-compatible and skin-attachable polydimethylsiloxane (PDMS) substrate, has been extensively conducted to monitor body health and environmental conditions.\cite{6} These advances have imposed pressure on the development of integratable power supply devices which have stable performance under deformation due to body movement. The miniaturized fMSCs with interdigitated structure, has the potential to be integrated onto the skin-type PDMS substrate. In Kim et al’s work, an array of nine CNT based fMSCs, individual sensors (a fragmentized graphene foam strain sensor and an MWNT/SnO\textsubscript{2} based NO\textsubscript{2}/UV sensor), and a wireless radio frequency (RF) power receiver were transferred onto a flexible and bio-compatible silicon Ecoflex substrate, and connected by embedded liquid metal lines (Fig. 14).\cite{6} The fabricated system could be attached to the skin and successfully detect biosignals, such as a neck pulse, saliva swallowing, voice and body movements and could provide a stable sensing signal upon exposure to NO\textsubscript{2} gas and UV light under a uniaxial strain up to 50%. Although further improvements (like pursuing higher output voltage of fMSC arrays and exploring matching components) are still required, this work shows the great potential of fMSCs in next-generation body-attached healthcare and environmental sensor systems.

6.3 Reference

[3] X. Tian, M. Shi, X. Xu, M. Yan, L. Xu, A. Minhas-Khan, C. Han, L. He, L. Mai,


