

Review

Recent progress in electrode materials for micro-supercapacitors

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SUMMARY

Micro-supercapacitors (MSCs) stand out in the field of micro energy storage devices due to their high power density, long cycle life, and environmental friendliness. The key to improving the electrochemical performance of MSCs is the selection of appropriate electrode materials. To date, both the composition and structure of electrode materials in MSCs have become a hot research topic, and it is urgent to compose a review to highlight the most important research achievements, major challenges, opportunities, and encouraging perspectives in this field. In this review, research background of MSCs is first reviewed followed by their working principles, structural classifications, and physiochemical and electrochemical characterization techniques. Next, various materials and preparation methods are summarized, and the relationship between the MSC performance and structure and composition of materials are discussed in depth. Finally, this review provides a comprehensive suggestion on accelerating the development of electrode materials to facilitate the commercialization of MSCs.

INTRODUCTION

With the emergence of portable technologies such as smart phones, implantable medical devices, and microsensors, their electrochemical energy storage components are similarly developing rapidly with a focus on miniaturization, integration, and flexibility^{1–3} toward use in field applications.⁴ Compared with traditional large-capacity power supply devices, micro energy storage devices are far more compatible with portable electronics due to small size and potential for high energy density.⁵ Therefore, the development of small energy storage devices matching with portable electronic products has become the development direction of the next generation of energy storage devices. To date, according to different charge storage characteristics, the available microscale energy storage units are divided into micro-batteries (MBs) and micro-supercapacitors (MSCs).⁶ Their total areal size can be in the millimeter or even the centimeter scale with a distance between two adjacent electrodes down to the micrometer scale. Contrary to MBs with low areal power density (<5 mW/cm²)^{7–9} and limited lifetime (<1000 cycles),^{10–12} MSCs can be fully charged or discharged in seconds, providing ultrahigh areal power density (>10 mW/cm²) and long cycle lifetime (>10000 cycles).¹³ Moreover, the diaphragm-free structure of MSCs can satisfy multidirectional high-efficiency ion diffusion while avoid the occurrence of short circuit.¹⁴ Additionally, they are safe to use, environmentally friendly, and easily compatible with wearable electronic fabrics and microelectronic integrated systems.¹⁵

As a result, the field of MSCs has thus developed into an important class of miniaturized electrochemical energy storage devices^{16,17} In the past decade, the MSCs have been well studied and Figure 1 displays the development status of MSCs. In 2006, Sung et al. reported the polypyrrole (PPy) based flexible MSCs on solidified hydrogel substrate by photolithography and electrochemical polymerization.¹⁸ Since then, more and more research was studied on diversified electrode materials for MSCs.¹⁹ In the recent years, multi-functional MSCs with composite electrode materials have been explored intensively for practical applications.^{20,21} For example, just in 2023, Huijie Zhou et al. prepared the NiCo-MOF@CoOOH@V₂O₅ nanocomposites for MSCs fabricated by 3D-printed, exhibiting a high area specific capacitance of 585 mF/cm² and energy density of 159.23 μW h/cm² (at power density = 0.34 m W/cm²).²²

Despite significant progresses have been achieved in device structures, integrated systems, and preparation methods, there are no reviews focused on various types of electrode materials for MSCs. In addition, although some reviews involved electrode materials,²³ they only focused on a particular class, such as graphite-based materials,²⁴ flexible materials,²⁵ or highly cross-linked porous polymers. Therefore, there is still a great need for a comprehensive review in time to introduce the latest developments in electrode materials for MSCs and compare their advantages and disadvantages, applicability, and scalable preparation methods. This review provides a critical overview of the latest research progress in electrode materials for MSCs. As illustrated in Figure 2, the first part briefly provides an overview for MSCs, including their working principles, structural classifications, and electrochemical characterization methods. Next, various preparation methods of electrode materials are summarized. Afterward, we particularly focus on the latest advances in electrode materials and further

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<https://doi.org/10.1016/j.isci.2024.108786>



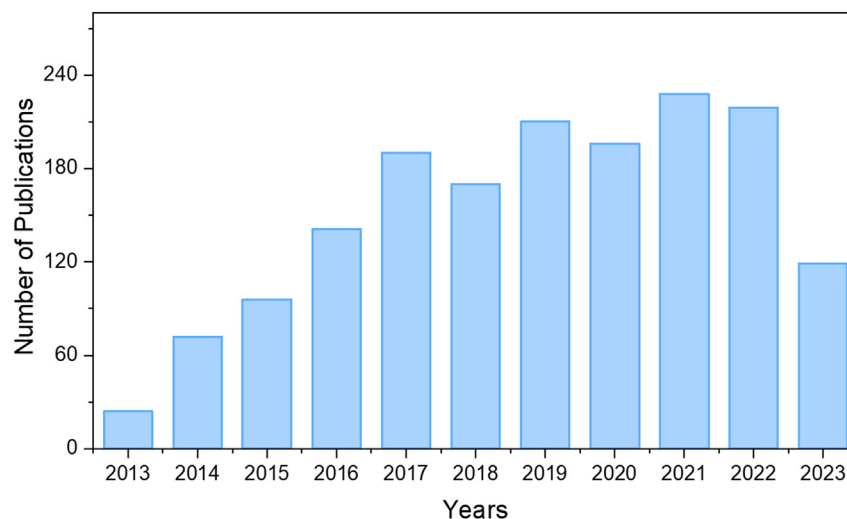


Figure 1. Number of publications on micro-supercapacitors according to the Web of Science (as of July 31, 2023)

introduce relationship between the MSCs performance and composition of electrode materials in depth. Finally, this review summarizes the future development and existing problems of MSCs.

OVERVIEW OF MICRO-SUPERCAPACITORS

MSCs are a class of supercapacitors that feature a smaller device size but operate by the same working principle as supercapacitors. Also known as electrochemical capacitors, supercapacitors are a new type of energy storage device that possess qualities of both batteries and traditional plate capacitors. Energy storage is achieved either through electrical double layer capacitance (EDLC),²⁶ which is generated by the adsorption and desorption process of charges on the electrode surface, or by the pseudo-capacitance generated by fast Faradaic reactions on the electrode material. The interfacial energy storage mechanism of supercapacitors requires a shorter time than battery materials for reversible redox reactions in the bulk phase, so supercapacitors possess higher power densities and excellent cycling stabilities.

According to the different energy storage mechanisms of electrode materials, supercapacitors can be divided into two main categories: EDLCs and pseudo-capacitors (also known as redox-type supercapacitors).

Working principle of EDLC

The EDLC operates on the principle that upon the application of an electric field to the positive and negative electrodes, they will attract oppositely charged ions in the electrolyte to form a charge layer, thereby establishing an electric double layer and realizing charge storage.²⁷ This principle is shown in Figure 3A. When the potentials applied to the two poles of the capacitor are different, the cations of the electrolyte will accumulate at the surface of the negatively polarized electrode material to balance the charge, while the anions will balance the positive electrode material. That is, the double layer exists at the interface between the electrode and the electrolyte ions. Through electrostatic adsorption, the positive and negative charges are separated, and charge layers of equal and opposite signs are generated to store energy. There is no charge transfer or redox reaction that occurs in this process, so the adsorption/desorption process at the interface can be rapid and the microstructure of the electrode material will not be damaged. This enables EDLCs to possess large power densities and long cycling lifetimes.

It can be seen from Equation 1 that the specific capacitance of the EDLC mainly depends on the specific surface area of the electrode material and the thickness of the electric double layer. Since the limited specific surface area is a bottleneck for its performance, development in this area has focused on the preparation of abundant pores. Carbon material electrodes are one such type and possess mesoporous high specific surface area and good electrical conductivity, including materials such as graphene, carbon nanotubes (CNTs), activated carbon, etc. Because increasing the specific surface area accessible to electrolyte ions can increase the number of charges adsorbed at the interface between the electrode and the electrolyte, higher porosity and surface area increase the ability of the electrode material to store charge.

Working principle of Faraday pseudo-capacitors

Pseudocapacitive capacitors refer to the energy storage generated by the highly reversible chemical adsorption-desorption or redox reactions of electroactive substances to store charges on the electrode surface and the near-surface bulk phase in two-dimensional or quasi-two-dimensional space. In the process of pseudocapacitive energy storage, charge transfer occurs, and the redox reaction of electrode materials occurs only in a specific potential range during the reaction process. Thus, specific capacitance is a potential-related variable, whereas for EDLCs there is no redox reaction and the specific capacity is independent of the potential. Pseudocapacitive supercapacitors have the

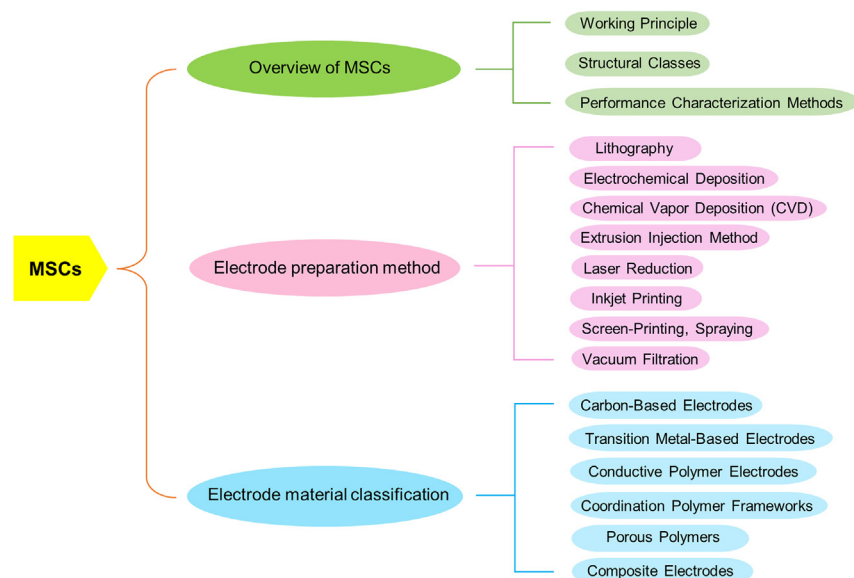


Figure 2. Flowchart of this review article structure

advantages of high capacitance and high energy density, but their redox reactions can be slow and Coulombic efficiency is low, so they can also suffer from low power density, slow rate capability, and short cycle life. Commonly used active materials are metal compounds (MnO_2 , $\text{Ni}(\text{OH})_2$, and NiCo_2S_4) and conductive polymers such as polypyrrole (PPy), polyaniline (PANI), and polythiophene (PTH).

B.E. Conway divided the Faraday pseudo-capacitor energy storage mechanism into three categories²⁸: underpotential deposition (Figure 3C), redox pseudo-capacitance (Figure 3D), and intercalation pseudo-capacitance (Figure 3E). The first is underpotential deposition, which is generally uncommon and occurs primarily on the surface of inert metals such as gold. It occurs by the application of certain metal redox overpotential to cause ionic adsorption to the inert metal surface; in other words, metal ions in the solution obtain electrons on the surface of another metal to form an adsorbed monolayer. The second is redox pseudo-capacitance, which occurs when ions are electrochemically adsorbed to or near the metal surface and is accompanied by Faradaic charge transfer, mostly in aqueous electrolytes; a typical material is ruthenium oxide. The third is the intercalation/deintercalation mechanism in which ions are intercalated into tunnels or interlayers with redox-active materials. This is also accompanied by Faraday charge transfer, but there is no crystal phase transition, which is common in non-aqueous electrolysis. In liquid systems, the corresponding electrode materials are mostly layered structures, so when electrolyte ions are inserted into the tunnel-like or layered material and the redox reaction occurs, the electrode material will not undergo phase change during this process.

While pseudo-capacitors will have a large amount of charge transfer when the redox reaction occurs on the surface or near the surface of the electrode material, only physical electrostatic adsorption occurs for the EDLC on the surface of the electrode material, so the specific capacity of pseudo-capacitor supercapacitors can exceed that of EDLCs by a factor of 10–100.²⁹

EDLCs and pseudo-capacitors are not mutually exclusive technologies and can be integrated with each other. Currently, a highly promising research direction is hybrid capacitors, or combining the two energy storage mechanisms of electric double layers and pseudo-capacitors in the same device.³⁰ Hybrid capacitors are expected to benefit from dual advantages to obtain energy storage devices with both high power and energy density.

Structural classes of micro-supercapacitors

The structures of MSCs are mainly divided into two types³¹: the traditional “sandwich structure” and the planar interdigitated structure, as shown in Figure 3B. The sandwich-type structure is layered between two electrodes with a separator or solid electrolyte, which is suitable for most electroactive materials and large-scale production with low cost and high yield. However, micro-devices with this electrode structure are prone to short-circuiting due to external impact during physical use and handling. Additionally, the distance between the two electrodes cannot be precisely controlled, and the electrolyte ions can only move in a unidimensional direction inside the electrode material. Large ion diffusion resistances will increase the internal contact resistance of the device, reduce the ionic conductivity, and reduce the electrochemical reaction efficiency, which in turn leads to attenuated surface capacitance of the device and a lower power density.

The planar interdigitated structure^{32,33} can be further divided into two-dimensional or three-dimensional planar interdigitated structures according to the spatial morphology of the electrodes. Due to limitations on the size of the device, the 2D planar micro-capacitor provides a lower capacity per unit area of active material, so 3D in-plane MSCs have been developed to compensate for the lack of area capacitance. However, excessively thick electrodes^{34–38} also greatly hinder the fabrication accuracy and microfabrication process, and lead to slow kinetic

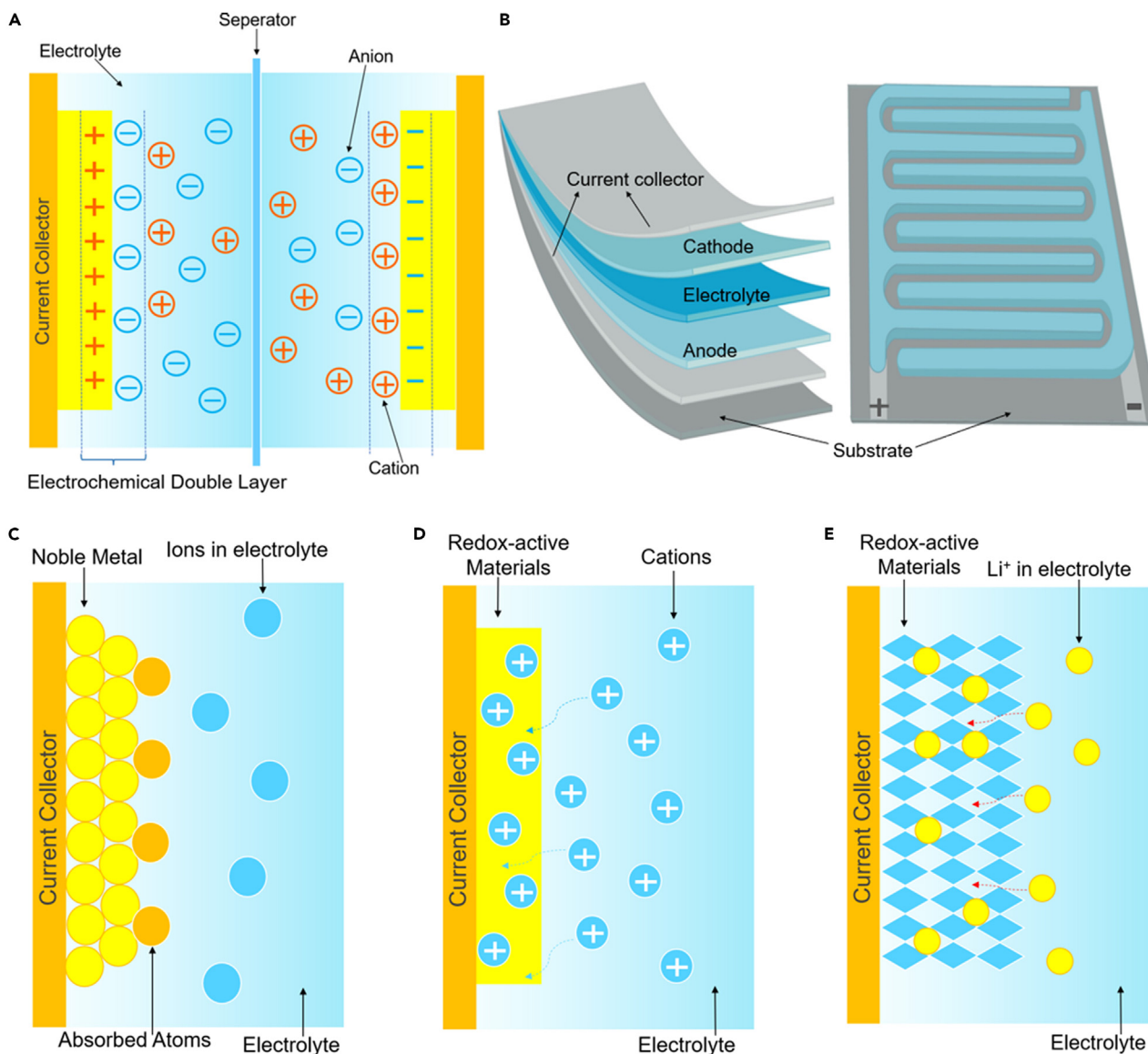


Figure 3. Principles and structures of electric double layer capacitors and pseudo-capacitors

(A) Principle of energy storage of electric double layer capacitors.

(B) Two structures of micro-supercapacitors, the traditional sandwich structure on the left and the planar interdigital structure on the right.

(C–E) Principle of energy storage of pseudo-capacitors.

behavior of MSCs. The positive and negative electrodes of the planar micro-capacitor are arranged in the same plane and separation between them is maintained. Therefore, liquid electrolytes such as aqueous or organic electrolytes and ionic dielectrics can be used. Since the distance between the interdigitated electrodes is fixed and no diaphragm is required, the device structure is simplified and the electrolyte ions can freely diffuse in 2D or 3D space. This ultimately shortens the diffusion distance of the electrolyte ions, reduces the transmission resistance of the electrolyte ions, and increases the contact area between the electrode material and the electrolyte. The characteristics of planar interdigital MSCs include ultrahigh power density, excellent rate performance, ultra-long cycle life and fast frequency response,³⁹ which are highly desirable for applications in modern electronic systems and makes this class of MSC a research hotspot in the field of micro-energy storage devices.^{31,40} Interdigitated electrodes can also be covered with solid electrolytes to meet the needs of different applications. In fact, many practical applications today are not compatible with the risk of electrolyte leakage, so solid electrolytes or gel electrolytes⁴¹ are preferred, such as polyvinyl alcohol (PVA) hydrogels mixed with standard aqueous or organic electrolytes ($\text{H}_2\text{SO}_4/\text{PVA}$, $\text{H}_3\text{PO}_4/\text{PVA}$, KOH/PVA , LiCl/PVA , etc.). Therefore, the planar interdigitated MSC is easy to integrate with micro-devices, and is also suitable for high-yield fabrication, making it the most-used MSC structure in current research.

Performance characterization methods

The capacitance performance of MSCs can be characterized by cyclic voltammetry (CV) or galvanostatic charge/discharge (GCD), the same way as supercapacitors, measuring charging and discharging processes of these devices.⁴²

The relative capacitance of the device can be calculated from the CV curve with the following formula⁴³:

$$C_A = \frac{1}{2v \times A \times (V_f - V_i)} \int_{V_i}^{V_f} I(V) dV \quad (\text{Equation 1})$$

$$C_V = \frac{1}{2v \times V \times (V_f - V_i)} \int_{V_i}^{V_f} I(V) dV \quad (\text{Equation 2})$$

where v is the voltage sweep rate (in V/s), V_i and V_f are the upper and lower voltage limits of the CV curve, $I(V)$ is the change in current with voltage (in A), A is the area of the electrode material (in m^2), and V is the volume of the electrode material (in m^3). C_A defines the relative area capacitance (in F/cm^2), while C_V is the relative volume capacitance (generally in F/cm^3). C_A and C_V can also be calculated from the GCD curve, the formula is as follows⁴³:

$$C_V = \frac{C_A}{d} \quad (\text{Equation 3})$$

$$C_A = \frac{J \times \Delta t}{\Delta V} \quad (\text{Equation 4})$$

where J is the current density of constant current charge and discharge (in A/m^2), Δt is the time of the discharge process, ΔV is the output voltage interval (in V), and d is the thickness of the electrode material.

The volume energy density (E , in Wh/cm^3) and power density (P , in W/cm^3) of MSCs can be derived from the relative capacitance of the device, which can in turn be calculated by the following formula⁴³:

$$E = \frac{1}{2} \times C_V \times \frac{(\Delta V)^2}{3600} \quad (\text{Equation 5})$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (\text{Equation 6})$$

PREPARATION PROCESSES

With the rapid development of MSCs, in order to adapt to different material characteristics and application fields, researchers have proposed various fabrication processes and methods.⁴⁴ These can be mainly divided into two categories: The first describes a general method that requires separate preparation of metal current collectors in addition to active materials, and includes photolithography, electrochemical deposition, chemical vapor deposition (CVD), extrusion injection, etc. This kind of method can be applied to a wide range of materials, since the precision and resolution of the resulting interdigitated structure of the device are high and the devices are easier to miniaturize. However, because an additional current collector preparation process is required, the process flow is not ideally simple. Additionally, since the current collector and active material are prepared separately, the binding stability between the two is also an important issue.

The second category of preparation method is to make the active material directly act as a current collector. Typical processes include laser direct writing, inkjet printing, screen printing and spraying, and vacuum filtration. This kind of method has the advantages of relatively simple processing, high preparation efficiency, and facile large-scale preparation of devices; however, the types of materials that can be applied to this kind of preparation method are relatively limited, and because there is no additional metal current collector, the performance of the overall device still has much room for further improvement.

Lithography

Including many etching techniques such as laser etching,^{45–48} electron beam etching, plasma etching, chemical etching, and photoresist stripping method, etc.,^{39,49–51} this method directly decomposes active materials to fabricate appropriately shaped interdigitated electrodes. They typically benefit a wide range of applications and can generate electrodes of small size and flexible design with high resolution. However, the material of interest needs to possess good etching selectivity to ensure that the electrode material is completely etched while the substrate retains its original properties.⁵²

Electrochemical deposition

By this method (including electrolytic and electrophoretic depositions), microelectrodes with interdigitated shapes are first evaporated on flexible substrates, and then electrode materials are vertically grown on the surface by *in-situ* electrochemical polymerization. This generates

a structure that is conducive to the full infiltration of electrolytes, thereby benefiting the electrode's performance. The effective active area of the material can direct the efficiency of charge transport. This method can avoid the subsequent steps of physical or chemical etching, and the preparation is typically more efficient,⁵³ but the types of materials that can be prepared are limited, mainly to conductive polymers.

Chemical vapor deposition (CVD)

Mature deposition methods have been extensively reported as the earliest fabrication techniques used in MSCs, besides the electrochemical deposition (referred in 3.2), CVD is particularly suitable for the growth of electrode materials based on chemical reactions. Microelectrodes can be directly obtained by depositing active materials on substrate, avoiding the use of binder additives. CVD is a commonly used method to evenly coat or deposit chemical species onto a surface or substrate of interest. It utilizes volatile chemical precursors that can be manipulated into the gas phase by careful control of temperature and pressure, which can be deposited more homogeneously onto a surface than is achievable with liquid solution dynamics or solid-solid interfacing. Desirable precursors include volatile organometallic complexes (a central metal atom coordinated by organic ligands), which are frequently coupled with subsequent thermal decomposition of the organic components to leave behind a uniform metallic thin film that can be further manipulated as an electrode material.⁵⁴

Extrusion injection method

First, metal current collectors (such as Au/Ti) with an interdigitated structure are evaporated on the substrate, and the positive and negative current collectors are separated by the curing and exposure decomposition of photoresist to form interdigitated grooves.⁵⁵ A hybrid MSC is formed by the dual electrodeposition of negative electrode materials (such as Zn nanosheets) onto the negative electrode surface and the injection of positive electrode materials (such as activated carbon slurry) into the positive electrode grooves. This method combines the battery-type negative electrode material and the capacitor-type positive electrode material, which not only helps retain the high-power characteristics of the supercapacitor, but also achieves a high area capacitance and has good cycling stability. Furthermore, such a process is not limited by the type of active material.

Laser reduction

The basic principle is the use of thermal reduction provided by a laser source to remove the oxygen-containing functional groups from the surface of graphene oxide to form reduced graphene oxide.^{56–59} The area affected by the laser becomes looser, more porous, and conductive reduced graphene oxide, while the unscanned area remains as non-conductive graphene oxide. This preparation method possesses low cost and simple processing,^{60–64} places few restrictions on the substrate material, and is capable of preparing interdigital electrode structures with complex patterns and shapes, which is beneficial to the mass production of MSCs. There are good application prospects in the field of flexible electronic devices. Another reported laser reduction method reduced polyimide films to graphene.^{65–68} The unreduced part is non-conductive and becomes the isolation part between the electrodes. In addition, the UV excitation method⁶⁸ is similar in principle to the laser direct method; both use a high-energy excitation source to force part of the precursor material to undergo a reduction reaction, thereby improving its conductivity.

Inkjet printing

Using commercial inkjet printers, interdigital electrodes can be accurately fabricated on a variety of substrates.⁶⁹ The surface tension, viscosity of the ink, and particle size of the target material are key factors that determine the success of inkjet printing for the fabrication of interdigital electrodes.^{40,62} Since inkjet printing can precisely control the pattern of electrodes by computer programming,⁷⁰ it is also possible to customize a suitable series/parallel array structure of MSCs according to the demand of the load on the output voltage or current. Solid-state flexible MSCs have good application potential in the field of integration with other electronic components prepared by inkjet printing or wearable electronics.

Screen-printing, spraying

Interdigitated electrodes can also be obtained by direct screen printing⁷¹ or spraying⁷² of the ink made of the electrode material onto the substrate using a mask. The preparation process is simple, low-cost, and has no restrictions on substrate materials, and can customize electrode patterns for large-scale production applications.^{71,72} Compared with the printing method, the spraying method does not have such high requirements on the viscosity and shear thinning of the slurry, so it is suitable for a wider variety of materials.

Vacuum filtration

This is a common method for preparing high-quality thin film materials. The interdigitated template is placed on a suction filter membrane and a suspension of the electrode material is filtered through^{73–75} to obtain electrodes of the desired shape. During the suction filtration process, the pressure from the air will be exerted on the top of the film, which is conducive to the uniform orientation of the internal materials and improves the compactness and flexibility of the film. The advantages of this method are low cost and simple operation, but there are many restrictions on electrode materials, and the resulting electrode size is on macroscale rather than microscale.

Table 1 summarizes various fabrication processes for different nanostructured electrode materials of MSCs.

Table 1. Comparison of various fabrication processes for different nanostructured electrode materials of MSCs

Type	Size of prepared electrodes	Requirements for electrode materials	Additional electrode preparation required?	Process complexity	Reference
Lithography	Small	Good etching selectivity	Yes	Complicated	Huang et al., 2015, Hwang et al., 2017, Shao et al., 2017, Wu et al., 2016 ⁴⁵⁻⁴⁸
Electrochemical Deposition		Conductive polymers			Moosavifard et al., 2016 ⁵³
Chemical Vapor Deposition		No requirement			Lin et al., 2013 ⁵⁴
Extrusion Injection					Zhang et al., 2015 ⁵⁵
Laser Reduction	Can be adjusted freely	Can improve its conductivity by reduction reaction	No	Relatively simple	El-Kady and Kaner, 2013, El-Kady et al., 2012, Liang et al., 2015, Zhao et al., 2017 ⁵⁶⁻⁵⁹
Inkjet Printing		Appropriate surface tension, viscosity of the ink			Shi et al., 2017 ⁶⁹
Screen-Printing, Spraying	Relatively large	Can customize electrode patterns			Guo et al., 2017, Liu et al., 2016 ^{71,72}
Vacuum Filtration		Many restrictions on electrode materials			Wu et al., 2017, Xiao et al., 2018, Xiao et al., 2017 ⁷³⁻⁷⁵

ELECTRODE MATERIALS

The properties of the electrode materials are the key to the preparation of high-performance capacitors. For micro-capacitors, designing new electrode materials with high specific surface area and high electrical conductivity within a limited space size is the focus and challenge for improving their electrochemical performance. The research on electrode materials is mainly centered in two aspects; one is to optimize the preparation method of the electrode material, which improves its physical and chemical properties, reduces the internal resistance of the electrode material, and ultimately improves performance benchmarks such as the specific capacitance of the electrode material. The second aspect is the study of novel electrode materials, expanding the scope of materials used in capacitors and continuously developing materials that improve their performance in critical applications.

At present, commonly used electrode materials for micro-capacitors mainly include carbon-based materials, metal compounds, conductive polymers,⁷⁶ coordination polymers,⁷⁷ porous polymers, and composite electrodes. Carbon-based materials exhibit high electrical conductivity and specific surface area, so micro-capacitors based on such materials have relatively high power density, rate capability, and cycle stability, but their energy density is often unsatisfactory. In contrast, metal compounds, polymer-based electrodes, and composite electrodes have a high density of redox active sites, which is conducive to a substantial increase in energy density, but are instead limited by low material electrical conductivity. This hinders their rate performance, cycle performance and frequency response performance.^{40,78}

Carbon-based electrodes

As a typical electrode material for EDLCs, carbon-based materials exhibit low cost, easy processing (controllable pore structure), good electrical conductivity (with some exceptions), high specific surface area, high temperature stability, and compatibility with other materials. These advantages have fueled the increased research of carbon-based electrode materials. Furthermore, oxygen-containing functional groups are easily generated on the surface of carbon materials, which then undergo reversible redox reactions in the electrolyte and enable the generation of Faradaic pseudo-capacitance, contributing greatly to the improvement of MSCs' specific capacitance. Typical carbon materials that are currently used to fabricate MSCs include graphene, CNTs or carbon fibers, activated carbon, carbide-derived carbon, and other EDLC materials.

Graphene

Due to its excellent electrical conductivity, electron mobility, ultrahigh specific surface area (2630 m²/g), high theoretical capacity (550 F/g), excellent film formation and unique two-dimensional structure, graphene has become a very useful electrode material. However, the number of inherent active storage sites is limited, which leads to insufficient energy and power density.

Commonly used methods for preparing graphene include CVD growth, liquid phase exfoliation, electrochemical exfoliation, and chemical reduction; however, the preparation processes often require expensive instruments, toxic and harmful reagents, or complex manipulation steps, making them unfeasible for large-scale applications. Among these graphene-related materials, reduced graphene oxide (rGO) has

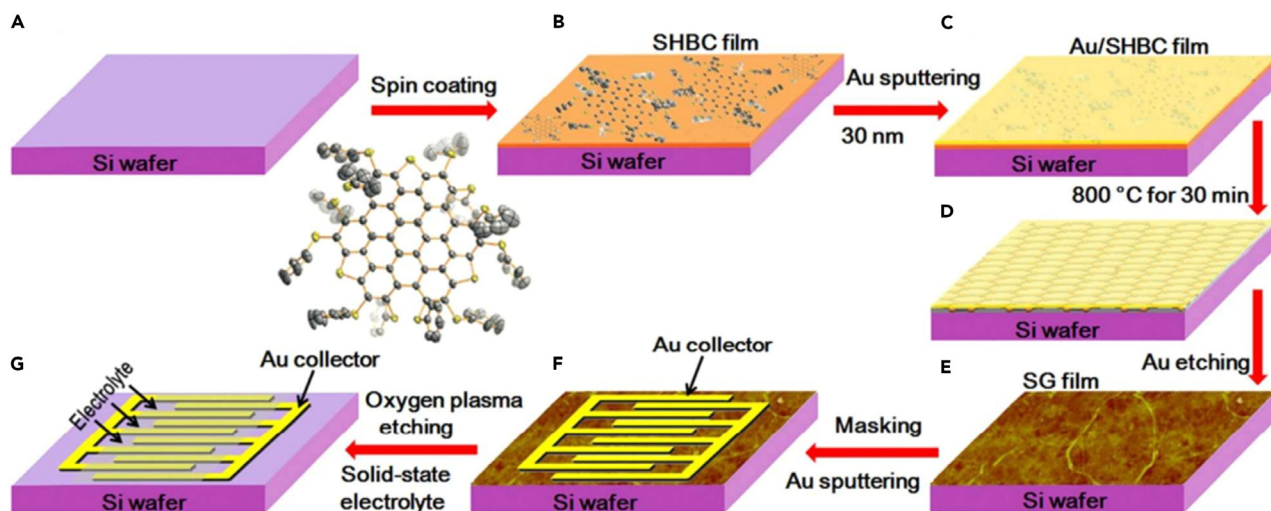


Figure 4. Schematic illustration of SHBC-derived SG films for planar MSCs on a Si/SiO₂ wafer

- (A) Spin-coating of the SHBC solution on surface-modified silicon with oxygen plasma treatment.
 (B) Sputtering Au with a thickness of 30 nm on the SHBC film.
 (C) Thermal annealing at 800°C for 30 min.
 (D) Au etching by a KI/I₂ aqueous solution.
 (E) Masking micropatterns and deposition of gold current collector.
 (F) Oxygen plasma etching and drop casting of H₂SO₄/PVA gel electrolyte on interdigitated fingers.
 (G) All-solid-state SG-MSCs obtained after solidification of gel electrolyte. Reproduced with permission from ref.⁸⁰ Copyright 2017 American Chemical Society.

become the most commonly used graphene-based electrode material for MSCs due to its simple preparation process, cheap and readily available raw materials, and abundance of electrochemical defect sites.

In 2013, Wu et al. reported a preparation method of micro-capacitors using rGO as an electrode material.⁷⁹ In this method, graphene oxide (GO) was first spin-coated on the surface of a silicon substrate to form a reduced graphene film (called an MPG film) and then subsequently reduced via methane plasma at 700°C. Next, an interdigitated gold current collector was vapor-deposited on the surface of the film by a masking and sputtering method. The remaining exposed graphene film was etched and removed, and finally micro-capacitor devices (MPG-MSCs) were fabricated. The thickness of the reduced graphene film prepared by this method was between 6 and 100 nm and can reach conductivities of 345 S/cm, relative area and volume capacitances of 80.7 μF/cm² and 17.9 F/cm³, respectively, and ultrahigh power density up to 495 W/cm³. In addition, the device also exhibited excellent cycling stability, with capacity retention of 98.3% after 100,000 cycles.

Such graphene films as electrode materials and flexible polyester (PET) films as substrates can also be utilized as excellent flexible MSCs. In order to further improve the performance of devices using graphene films as electrode materials, in 2017, Wu et al. also prepared a planar MSCs based on sulfur-doped graphene films (SG-MSCs) (Figure 4).⁸⁰ The SG-MSCs exhibited excellent capacitive performance, and their C_v could reach an ultrahigh 582 F/cm³, which was the highest value among carbon-based MSCs before 2017.

Carbon nanotubes (CNTs)

CNTs are a new type of one-dimensional carbon-based electrode material, which can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). They possess high surface area and excellent film-forming properties, with unique pore structure, high electrical conductivity, good mechanical flexibility, and high thermal stability.^{81–83} Electrode materials composed of aligned CNTs exhibit better electrochemical performance than those of randomly distributed CNTs due to the improved contact between the electrode and the electrolyte, the decreased diffusion distance of electrolyte ions, and ultimately promoting rapid electron transport and higher electrochemical reaction efficiency. However, since the van der Waals force between the CNTs and the substrate is a weak physical interaction force, the contact internal resistance between the electrode material and the substrate is likely to increase during use; or, alternatively, the CNTs may even become detached from the substrate entirely, which eventually leads to a short cycle life. The typical strategy employed to overcome this is the introduction of conductive polymers or other pseudocapacitive materials, which can not only increase the bonding force between the electrode material and the substrate but also introduce pseudo-capacitance to the material. This synergistic effect helps to improve the energy and power density of CNT-based composite electrode materials.

In 2002, Hughes et al. coated a layer of polypyrrole (PPy) on the surface of vertically oriented MWCNT by electrochemical polymerization to obtain an MWCNT-PPy composite thin film electrode. The electrochemical test results showed that not only is the cycle life of MWCNT-PPy significantly improved, but so is the specific capacity, reaching 2.55 F/cm² in stark contrast to that of the pure PPy (0.62 F/cm²).

In 2014, Braun et al. reported a method to fabricate MWCNT-based interdigital micro-capacitors by slurry injection.⁸⁴ The method used polydimethylsiloxane (PDMS) to prepare an interdigitated groove structure template, dispersed MWCNTs in water to prepare slurry, and then injected the slurry into the interdigitated groove. Polyvinyl alcohol/phosphoric acid (PVA/H₃PO₄) was then cast as a solid electrolyte, and the PDMS/cured electrolyte film were finally stripped and then connected with copper tape as a wire connection to obtain planar MSCs. The device exhibited a volumetric capacitance (C_V) of about 5.0 F/cm³ at a discharge current of 0.009 A/cm³ as well as excellent cycling stability, with a capacity retention of about 98% after 10,000 cycles.

The same year, Wei et al. used CNT and chitosan to prepare a yarn-like composite material by a wet spinning method. After high-temperature treatment, a yarn-like SWNT@C material was obtained, and an integrated microfabricated SWNT@C material was prepared.⁸⁵ The SWNT@C material exhibited excellent electrical conductivity, reaching up to 601.8 S/cm. The full micro-capacitors based these yarn electrodes further demonstrated excellent cycling stability, with only about 1.5% capacity loss after 10,000 cycles of constant current charge-discharge. In addition, the device had an energy density of 3.7 mWh/cm³ and was capable of powering a light-emitting diode (LED). CNTs are exceptionally flexible and ductile, so CNT-based micro-capacitors can be made with excellent mechanical stability.

In the same year in 2014, Ha et al.⁸⁶ deposited CNT thin films on interdigitated current collectors by layer-by-layer self-assembly method; then, the obtained micro-capacitors were integrated and assembled, and the final micro-capacitor integrated system showed double axial scalability, which has great application potential in wearable flexible electronic systems.

In 2016, Sun et al.⁸⁷ used a plasma-enhanced chemical vapor deposition (PECVD) process to prepare vertical arrangement carbon nanotubes (VACNTs) on interdigitated electrodes, and then introduced MnO₂ nanoparticles by electrochemical deposition, forming MSCs with MnO₂/VACNT composite electrodes. Tests in aqueous electrolyte of 0.5 M Na₂SO₄ demonstrated that with a scan rate of 50 V/s, the specific area capacity of this MnO₂/VACNT-based MSC can reach 24.0 mF/cm², which is 40 times improved from that of the pure VACNT MSC, and the cycling stability of the device is improved as well.

Activated carbon

Activated carbon⁸⁸ utilizes cheap and readily available raw materials and features high specific surface area (ranging from 500 to 3000 m²/g), good electrochemical stability, and adjustable porosity (pore size distribution is 0.9 nm–1.5 nm). Due to these benefits, this electrode material is commonly used in commercial supercapacitors^{87,89} and is generally prepared by heat treatment or chemical activation.

In 2010, Pech et al.⁸⁸ prepared MSC devices by electrophoretic deposition of activated carbon. In 1 M Et₄NBF₄ organic electrolyte, the specific capacity was lower than 5 mF/cm², indicating that the prepared microdevices had a lower relative area capacitance.

Gogotsi et al.⁹⁰ used sputtering deposition and chlorination to prepare a TiC film into a conductive, porous CDC (carbide-derived carbon) film, and then used a dry etching method to prepare a planar interdigitated micro super film. Electrochemical tests in organic electrolytes showed a specific capacity of 180 F/cm³, and when alternatively tested with 1 M H₃PO₄ as electrolyte, the specific capacity measured at a scan rate of 20 mV/s was 160 F/cm³.

The same year, Simon et al. reported a planar micro-capacitor based on “onion-like” carbon materials.⁹¹ The preparation of such activated carbon materials required annealing nanodiamonds at a high temperature of 1800°C, followed by deposition of carbon nanoparticles on the surface of interdigitated gold current collectors by electrophoretic deposition to obtain micro-capacitive electrode films. This “onion-like” carbon material had excellent electrical conductivity with a specific surface area of about 500 m²/g, and it can be deposited directly on the current collector without an organic binder. The resulting micro-capacitor exhibited excellent cycling stability (up to 10,000 cycles) and rate capability; the specific area capacitance (C_A) can reach 0.9 mF/cm² at a scan rate of 100 V/s and remain higher than the C_A values of many EDLCs at lower scan rates (1–100 mV/s), fully demonstrating the application advantages of such carbon materials as electrode materials in planar MSCs.

In 2011, Shen et al.⁹² reported a method to fabricate silicon-based MSCs using activated carbon as an electrode material by photolithography. Tests in 1 M NaNO₃ aqueous electrolyte showed that when the scan rate was 50 mV/s, the specific capacity calculated from the CV curve reached a maximum of 90.7 mF/cm², and the prepared activated carbon electrode displayed robust electrochemical properties.

In 2011, Beidaghi et al.⁹³ first used photoresist to prepare two-dimensional planar interdigitated electrodes, which were carbonized at 1000°C to obtain MSCs using activated carbon as electrode material. The specific capacity measured at 5 mV/s was 75 mF/cm², and the specific capacity still retained 87% after 1000 cycles of testing.

Transition metal-based electrodes

Transition metal-based electrode materials refer to compounds such as transition metal oxides,^{94–97} hydroxides^{98,99} carbides,¹⁰⁰ nitrides,^{90,101} and sulfides^{102–105}; some specific examples include RuO₂, MnO₂, NiO, Co₃O₄, NiS, CoS₂, Co₉S₈, NiCo₂O₄, and NiCo₂S₄.

The surface of transition metal compounds are capable of undergoing rapid redox reactions and can provide high pseudocapacitive capacity and increased energy density, making transition metal compounds an important electrode material for the preparation of micro-capacitors.¹⁰⁶ However, their relatively low electrical conductivity (compared to carbon materials) and poor cycling stability limit their application in MSCs. In order to further improve the cycle stability of transition metal compound electrode materials, materials with higher specific surface area are generally introduced (such as carbon materials or conductive polymers) in order to prepare composite electrode materials. The dual use of electric double layer electrode materials with high power, long cycle life, and pseudocapacitive electrode materials with high specific volume can synergistically improve the energy storage properties of their composites.^{82,107–109}

Transition metal oxides

Transition metal oxides commonly used in micro-capacitor electrode materials include RuO₂, MnO₂, and NiO. The electrical conductivity of RuO₂ is two orders of magnitude higher than that of carbon materials, and RuO₂-based micro-capacitors also have better capacitive performance than those of carbon materials. Additionally, the RuO₂ electrode is stable in sulfuric acid solution, so it was the first and most studied transition metal oxide-based electrode material. However, due to its high price and environmental unsustainability, it is only used for laboratory research at present and cannot produce practical application value. Therefore, researchers have explored alternative metal oxides such as MnO₂, NiO, etc., which have similar capacitance properties to RuO₂ and are less expensive. MnO₂ is cheap, non-toxic, and non-polluting, and when used as a micro-capacitor electrode material for electrochemical tests, it displayed excellent capacitance characteristics and a wide electrochemical window. As discussed in previous sections, composite electrode materials featuring MnO₂ and some added carbon materials also demonstrated a high performance. Therefore, this electrode composition has attracted extensive attention from researchers worldwide.^{110,111}

In 2012, Liu et al.¹¹² used the interface exchange mechanism to prepare a three-dimensional MnO₂-NiO nanotube array composite electrode with ZnO as a sacrificial template. When the current density was 5 mA/cm², the specific capacity was 0.4 F/cm², and after 1500 cycles the specific capacity retained 87.5% of its original value with a Coulombic efficiency of 96%.

In 2013, Sugimoto et al. reported a preparation method of planar micro-capacitors based on ordered mesoporous ruthenium oxide (RuO_x).¹¹³ First, the metal Ru film was deposited on current collector with interdigitated shape by electrochemical deposition, and the soluble crystalline material was used as a template during the deposition process to form an ordered pore structure. Subsequently, metal Ru film was electrochemically oxidized to RuO_x, forming materials with ordered mesoporous structure. Benefiting from superior pseudocapacitive properties of RuO_x, the specific area capacitance (C_A) of the fabricated micro-capacitors reached up to 12.6 mF/cm².

In 2013, Schmidt et al. prepared a MnO_x/Au multilayer thin film electrode material by electron beam deposition.¹¹⁴ In this multilayer structure, an extremely thin Au layer was embedded between the MnO_x layers, effectively facilitating the transport of electrons inside the electrode material. The planar micro-capacitor based on this electrode material still maintained a high C_V (32.8 F/cm³) at a high scan rate (1 V/s).

In 2017, Lin et al.⁷⁰ fabricated MnO₂ flexible solid-state MSCs on PET substrates by inkjet printing and electrochemical deposition processes. The specific capacity of the microdevice was 52.9 mF/cm² with a scan rate of 5 mV/s. After 500 cycles of testing at 180° bending, the specific capacity retention rate was 77.4% and the Coulombic efficiency was 80%, indicating the cycling stability of the microdevice was significantly attenuated. During the process of electrolyte ion embedding/detachment inside the electrode material, the internal structure of MnO₂ was damaged, which in turn reduced the electrochemical performance of their microdevices.

In 2018, Zhai et al.⁹⁷ used a hydrothermal reaction and annealing process to prepare a fibrous holey graphene oxide (HGO)/RuO₂ solid-state MSC with a specific capacity of 199 F/cm³ at a scan rate of 2 mV/s. The highest energy density of the micro device reached 27.3 mWh/cm³ (corresponding power density of 147.7 mW/cm³), and its specific capacity retention rate was 78.7% after 10,000 cycles, retaining a Coulombic efficiency as high as 98%.

Transition metal hydroxides, sulfides, carbides, and nitrides

In addition to transition metal oxides, other metal compounds with good film-forming properties have also been used to fabricate micro-capacitors, including transition metal hydroxides, sulfides, carbides, and nitrides.

MXene is a two-dimensional transition metal carbide, of which Ti₃C₂T_x is a typical representative, that exhibits high electrical conductivity and high theoretical capacity and is a popular micro-capacitor electrode material. In 2016, Gogotsi et al. reported an all-solid-state micro-capacitor entirely based on Ti₃C₂T_x (Figure 5), where Ti₃C₂T_x was both an active material and a current collector.¹⁰⁰ First, the Ti₃C₂T_x suspension was prepared by acid etching and ultrasonic-assisted methods, and then the Ti₃C₂T_x slurry was uniformly sprayed on the surface of the glass sheet to form a thin film. The interdigitated structure of this thin film material was obtained by laser beam cutting. Finally, PVA/H₂SO₄ was selected as the electrolyte and is dropped and cured on the surface of the film, forming the full solid-state micro-capacitor. This device exhibited excellent capacitive performance, with area capacitance (C_A) up to 27.3 mF/cm² and volume capacitance (C_V) reaching an ultrahigh value of 356.8 F/cm³ at a scan rate of 0.2 mA/cm². In addition, it also exhibited particularly excellent cycling stability, with a capacity retention rate of 100% after 10,000 CV cycles. Other planar micro-capacitors using metal carbide-derived electrode materials also revealed excellent electrochemical performance,⁹⁰ demonstrating a C_V of up to about 160 F/cm³.

Two-dimensional transition metal dichalcogenides have also become a popular field for the fabrication of planar micro-capacitors due to their unique physical properties. In 2013, Ajayan et al. prepared a micro-capacitor based on molybdenum disulfide (MoS₂) nanosheets¹¹⁵ with a preparation method similar to that of Ti₃C₂T_x-based MSCs, in which the MoS₂ slurry was sprayed on the surface of the silicon substrate and etched by a laser probe to obtain the interdigitated structure. The resulting micro-capacitors had a C_A of up to 8 mF/cm² and a C_V of up to about 180 F/cm³. Xie et al. also reported a class of micro-capacitors using vanadium disulfide (VS₂) as the electrode material.¹¹⁶ They deposited a strip-like VS₂ film on the substrate by mechanical means, followed by a gold layer for use as a current collector, and used an organic ionic liquid as an electrolyte to obtain a micro-capacitor device. The C_A and C_V of this device could reach 4.76 mF/cm² and 317 F/cm³, respectively, without obvious capacity loss after 1000 charge-discharge cycles.

In 2014, Xiao et al.¹¹⁷ first prepared NiCo₂S₄ nanotubes and NiCo₂O₄ nanorod electrode structures on carbon fiber cloth. When the current density was 4 mA/cm², the specific capacity of NiCo₂S₄ electrode was 0.52 F/cm², while that of NiCo₂O₄ electrode was 0.40 F/cm². The electrochemical test results showed that the NiCo₂S₄ electrode material had better electrochemical performance. Subsequently, a layer of Co_xNi_x(OH)₂ nanosheets was electrochemically deposited on the surface of the NiCo₂S₄ nanotube electrode to form a Co_xNi_x(OH)₂/NiCo₂S₄

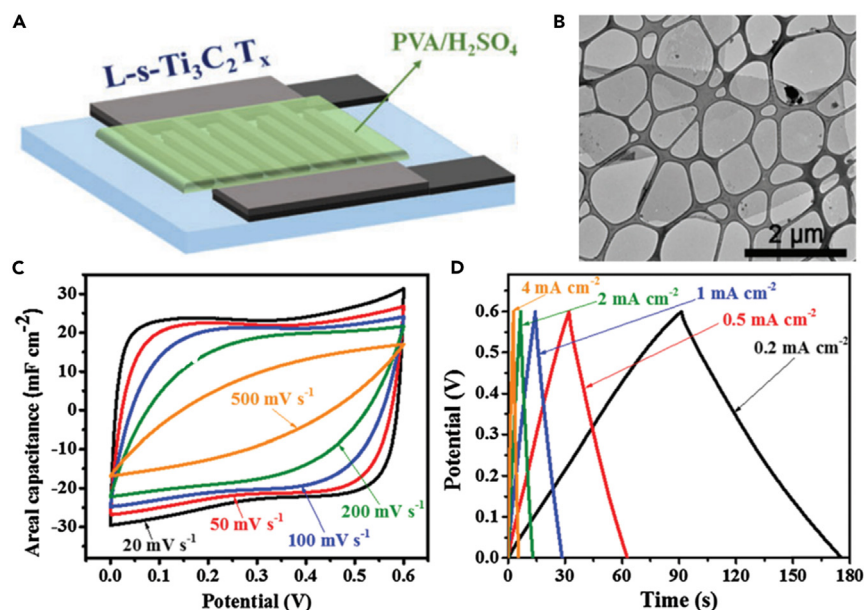


Figure 5. MSCs based on MXene

(A) Schematic illustrating the all- $\text{Ti}_3\text{C}_2\text{T}_x$ MXene MSC.

(B) TEM micrographs showing individual L- $\text{Ti}_3\text{C}_2\text{T}_x$.

(C) CV curves of the L- $\text{Ti}_3\text{C}_2\text{T}_x$ MSC at different scan rates.

(D) Charge-discharge profiles of the L- $\text{Ti}_3\text{C}_2\text{T}_x$ MSC at different current densities. Reproduced with permission from ref.¹⁰⁰ Copyright 2016 Royal Society of Chemistry.

composite structure. When the current density was 4 mA/cm^2 , the specific capacity was as high as 2.86 F/cm^2 , and the specific capacity retention rate was 96% after 2000 cycles. This is because NiCo_2S_4 nanotubes with high electrical conductivity not only provided three-dimensional conductive channels in composite electrode materials to promote rapid electron transfer and increase the contact area between electrode and electrolyte, but also greatly improved the composite electrode as a pseudocapacitive material.

Conductive polymer electrodes

Common conductive polymers include materials such as polyethylene (PE), polyaniline (PAN), polypyrrole (PPy), polyacene (PAS), polypara-phenylene (PPP), poly-3,4-ethylenedioxythiophene (PEDOT), polythiophene (PTh), and their derivatives. Conductive polymers possess high electrical conductivity, large specific capacity, and good electrochemical reversibility, making them a promising class of energy storage materials.^{118–120} MSCs utilizing conductive polymers as electrode materials have high energy storage density (10–100 times that of carbon materials and metal oxides), because conductive polymers are composed of alternately arranged single and double bonds. This forms a π -bonded conjugated structure and can store charges through the highly reversible doping/de-doping reaction between the polymer molecular chain and the electrolyte ions, which belongs to the pseudocapacitive energy storage class of materials. Conductive polymers also benefit from a relatively high working voltage (greater than 3.0 V), with the use of a non-aqueous working electrolyte. In addition, conductive polymers have good mechanical flexibility, low toxicity, low cost, and facile preparation methods (electrodeposition is frequently used), so they are widely used as electrode materials for MSCs.^{121–123}

Polyaniline (PANI)

Polyaniline (PANI) is a class of easily synthesized and low-cost electrode materials, so the resulting microelectronic systems have great potential for practical applications.^{124,125} In 2014, Irazoqui et al. reported a preparation method of flexible micro-capacitors using PANI as the active material.¹²⁶ They used the electrodeposition method to directly grow PANI on the front and back sides of the current collector, making full use of the area surrounding the current collector. The C_V of a PANI-based micro-capacitor device reached up to 105 F/cm^2 and the energy density was up to 7.4 mWh/cm^3 . In addition, this micro-capacitor can be used as a device module to be connected in series or in parallel to achieve a highly integrated, adaptable array toward a variety of application scenarios.

Polypyrrole (PPy)

Polypyrrole (PPy) is also a common supercapacitor electrode material. PPy has good electrical conductivity, but MSCs using PPy as electrode materials generally suffer disadvantages of small specific capacity and poor cycling stability. In 2013, Zhou et al.¹²⁷ loaded pyrrole monomer on the surface of ordinary printing paper by infiltration method and obtained PPy-coated flexible paper by oxidative polymerization. Then,

cutting and assembly were performed to finally obtain a PPy-based planar micro-capacitor. The as-prepared PPy-coated paper showed excellent flexibility and possessed good electrical conductivity of 15 S/cm, energy density of 1.0 mWh/cm³ as an electrode material, and a capacity retention rate after 10,000 cycles of 75.6%.

Poly-3,4-ethylenedioxythiophene (PEDOT)

Due to the higher molecular weight of EDOT monomer and the lower doping rate, the specific capacity of PEDOT is lower than that of PANI and PPy, but the P-type doping of PEDOT is different in various electrolytes (aqueous, organic, and ionic liquid). With high electrochemical activity and wide voltage window, PEDOT has become the most studied class of conductive polymer electrode materials.¹²⁸ In 2014, Meng et al. used photolithography to prepare current collectors with interdigitated patterns, electrochemically polymerized PANI micro interdigitated electrode materials on them, and assembled them together with H₂SO₄/PVA gel electrolyte to form an all-solid MSC. When the current density was 20 mA/cm², the specific capacity of the device reached 16.5 mF/cm², and the specific capacity retention rate remained at 87.6% after 2000 cycles.

In 2015, Kurra et al.⁸⁹ used traditional photolithography and electrochemical deposition to prepare PEDOT MSCs, which achieved a maximum area specific capacity in 1 M H₂SO₄ aqueous electrolyte of 9 mF/cm² and a corresponding volumetric capacity of 50 mF/cm³. After 10,000 cycles of testing, the specific capacity remained at 80% of its original value, and the Coulombic efficiency was close to 100%.

Composite conductive polymers

A large number of research studies show that the electrical conductivities of PANI, PPy, PTh and their derivatives are still low compared to carbon-based materials, and the specific capacities of their respective prepared electrode materials in aqueous/non-aqueous electrolytes are on the order of 150–190 F/g, 80–100 F/g and 78–117 F/g; thus single-constituent conducting polymers generally demonstrate a relatively low specific capacity that cannot meet practical needs.¹²⁹ In addition, conductive polymer electrode materials can experience shrinkage/expansion during the doping/de-doping process. After long-term cycle tests, the structures of polymer molecular chains are damaged and collapse, eventually leading to decay of cyclic stability. Therefore, many researchers have attempted to introduce porous conductive networks or nanosheet structures to improve the stability of conductive polymer structures and their energy storage properties.¹³⁰

In 2014, Meng et al.¹³¹ used electrochemical polymerization to deposit polyaniline nanowires (PANINWs) on the surface of SWCNT fibers to prepare fibrous SWCNT/PANINW composite electrodes, using PVA/H₂SO₄ gel electrolyte to assemble all-solid-state MSCs. The specific capacity of the SWCNT/PANINW microdevices was measured to be 6.23 mF/cm² at 0.2 A/g, while the specific capacity of the single SWCNTs microdevice was only 0.34 mF/cm². Further, after 800 cycles, the specific capacity retention rate was 86%, showing good cycle stability.

In 2016, Sun et al.¹³² used electrodeposition to prepare both PEDOT/MnO₂ and C/Fe₃O₄ composite electrodes separately and then assembled them together with PVA/LiCl gel electrolyte to form a solid-state asymmetric MSC. The operating voltage window of this micro-device can be extended to 2 V. When the current was 0.9 mA, the specific capacity reached 60 mF/cm², the corresponding energy density was 0.0355 mWh/cm², and the capacity remained 80% after 800 cycles.

Coordination polymer frameworks

Coordination polymer frameworks (CPF) have a molecular framework structure that is conducive to the insertion and extraction of charges and is an emerging electroactive organic polymer micro-capacitor electrode material. CPFs belong to the class of coordination compounds, generally composed of transition metals as central atoms and organic units as connecting ligands, which interact by coordination bonds. They are marked by neat molecular framework structures and nanopores or channels, high relative void spaces, and abundant metal atoms for chemical activity; for instance, the central atom can act as a potential redox site. In addition, these materials are highly tunable, with both the metal atom identity and the connecting ligand species capable of influencing the chemical properties and physical morphology of the materials. In recent years, CPFs as a new type of “organic-inorganic” hybrid functional materials have aroused strong interest of researchers, and with the increased efforts in this area, more and more favorable properties are being discovered and developed.

In 2017, Yang reported the first micro-capacitor based on CPF material called Pi CBA (Figure 6A).¹³³ First, the interdigitated gold current collector was evaporated on the silicon substrate to obtain microelectrodes. After current collector surface was molecularly functionalized, the microelectrodes were alternately immersed in the reaction monomer solution, growing Pi CBA layers on the electrode surface. The selected ligand is a fused aromatic hydrocarbon structure containing five-membered rings and seven-membered rings. Theoretical calculations showed that the structure has a permanent dipole moment, an ultralow band gap, excellent carrier mobility (5×10^{-3} cm²/Vs), a conductivity of 2.4×10^{-4} S/cm, and was ultimately an excellent electrochemically active material. Using PVA/H₂SO₄ as the electrolyte, the obtained micro-capacitors based on pure coordination polymers had a C_v of up to 34.1 F/cm³ and a power density of 1323 W/cm³; these devices also exhibited outstanding AC linear filtering performance. The electrochemical impedance spectroscopy (EIS) measurement showed that its phase angle at 120 Hz could reach -73° , and its filtering performance was 87% of that of an ideal capacitor.

The most widely used CPFs in terms of MSC is metal-organic frameworks (MOFs). MOFs are a relatively new type of crystalline coordination polymer frameworks, which are connected by organic bridging ligands and central metal ions or central clusters through highly directional coordination bonds. Compared with traditional coordination polymer materials, MOF materials have many novel features, such as high crystallinity, precise chemical structure, long-range ordered pore structure, ultrahigh specific surface area, and potential for accessible, unsaturated active sites within the lattice. These unique properties allow MOF materials to exhibit extremely rich structural and functional diversity.¹³⁶ However, as the current research on MOF materials is still at an early stage, there are still some significant shortcomings. For

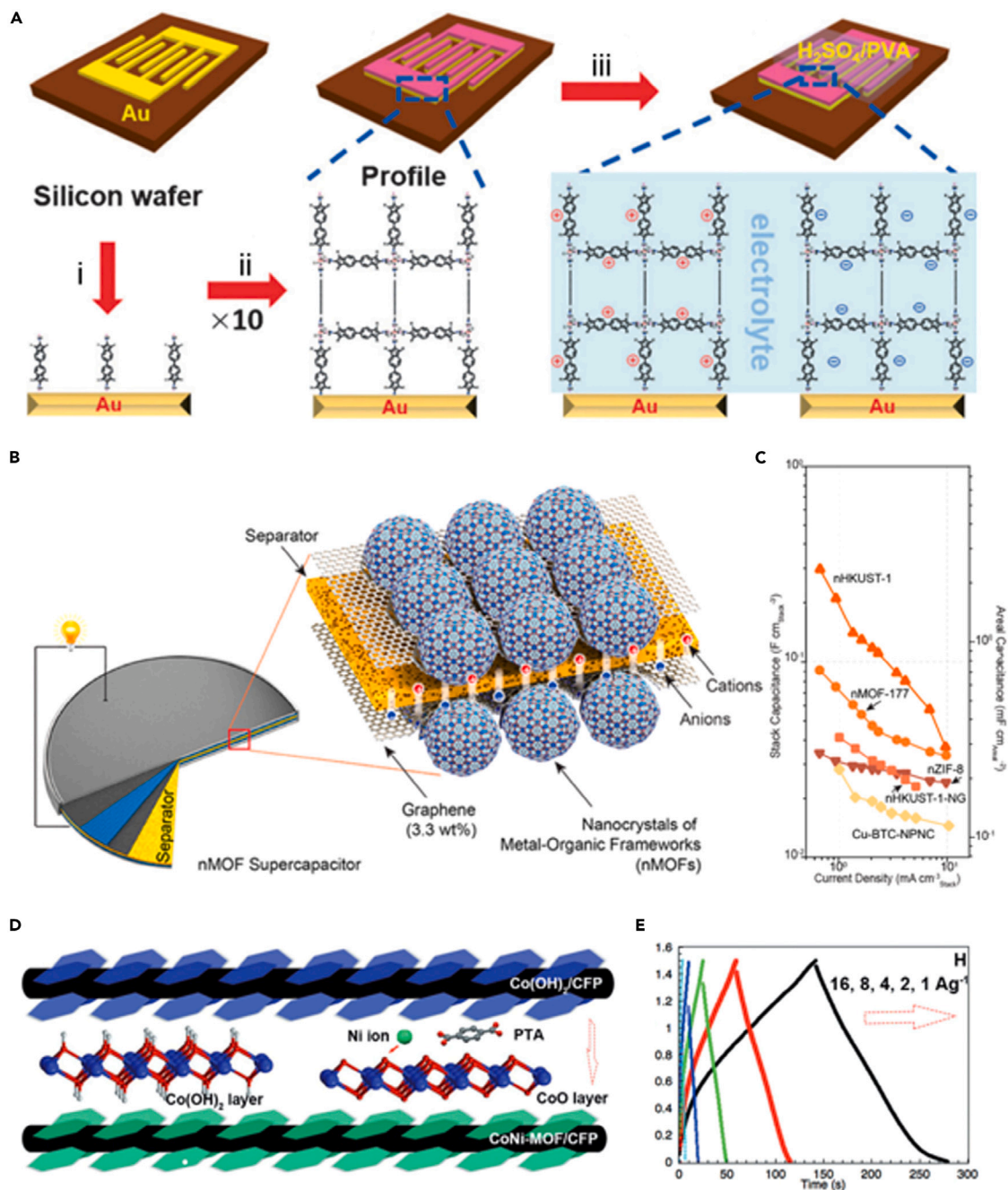


Figure 6. Fabrication and performance of an in-plane MSC based on PiCBA

(A) Schematic of fabrication of an in-plane MSC based on the coordination polymer framework PiCBA. (i) The Au interdigital electrode was immersed in iCBA solution for 24 h, followed by rinsing in fresh $CHCl_3$ and then (ii) immersed in $CoCl_2$ solution for another 60 s, followed by rinsing in DI water, iCBA solution for 60 s, and fresh $CHCl_3$, respectively, to form the 1-layer PiCBA film. This process was repeated nine times to obtain a 10-layer PiCBA-Au electrode. Reproduced with permission from ref.¹³³ Copyright 2017 Wiley-VCH.

(B) Construction of nMOF supercapacitors.

(C) Volumetric stack and areal capacitance of nMOFs and related supercapacitors. Reproduced with permission from ref.¹³⁴ Copyright 2014 American Chemical Society.

(D) The schematic illustration of $Co(OH)_2$ used as both the template and precursor for *in situ* synthesis of CoNi-MOF.

(E) Galvanostatic curves of the supercapacitor based on CoNi-MOF at different current densities. Reproduced with permission from ref.¹³⁵ Copyright 2017 WILEY-VCH.

example, many coordination bonds connecting metal ions and organic ligands are weak (e.g., sensitive to hydrolysis, aerobic conditions, strongly acidic or basic conditions, etc.), leading to poor functional stability of many MOFs. Despite these challenges, MOFs have demonstrated ultrahigh specific surface area and ordered rigid porous frameworks, allowing substrate accessibility and functional use, and the added chemical contribution of the metal atoms make them highly suitable for use as electrode materials in the field of energy storage.

In 2014, Yaghi et al. investigated the application of 23 MOF materials in supercapacitors (Figures 6B and 6C).¹³⁴ They first prepared the pristine nanocrystalline MOF powder, and then mixed the MOF with a small amount of graphene and spin-coated it on a clean substrate to obtain a thin film. Using an organic ionic liquid as the electrolyte, a separator was added between the two thin films to encapsulate it into a "button capacitor." The final results showed that among the 23 MOF materials, the supercapacitor with nMOF-867 as the electrode material had the highest relative area capacitance (reaching 5.085 mF/cm²), and the cycling life could exceed 10,000 cycles. In addition, nHKUST-1, nMOF-801, and nUiO-66 also exhibited excellent capacitive performance, with device C_A of 2.334 mF/cm², 2.329 mF/cm², and 1.945 mF/cm², respectively.

In 2018, Zheng et al. used Co(OH)₂ grown on the surface of carbon fiber cloth as both a precursor and a template to prepare a highly oriented CoNi-MOF containing two metal elements (Figure 6D and 6E).¹³⁵ The supercapacitor containing the MOF as the positive electrode and activated carbon as the negative electrode reached a maximum capacity of 1,044 F/g, and the capacity maintained at 94% after 5,000 charge-discharge cycles. At the same time, this work also proved that compared with traditional MOF powder materials, MOF films grown directly on the surface of the current collector can effectively improve the capacitance performance of this material, which provides a new research area on MOF-based supercapacitors.

The continued improvement of the conductivity of MOF materials is the core of promoting their further application in the field of MSCs. Additional efforts are also being applied to increasing the processability of MOFs, as MOFs generally exist in micropowder or crystalline states which is disadvantageous in the preparation of electrode films suitable for planar MSCs. The improved integration of powder materials into high-quality and controllable thin film materials is a required development if MOFs are to be successfully applied in the field of planar MSCs.^{137,138} Toward these efforts, in 2016, Takahashi et al. reported a heteroepitaxial preparation method for MOF film.¹³⁹ As shown in Figure 7, they first deposited a metal Cu film on a silicon wafer, and then immersed the Cu film in a mixture of sodium hydroxide and sodium persulfate to convert Cu into Cu(OH)₂. This was followed by immersion in a solution containing the terephthalic acid ligand, converting the material into a Cu₂(BDC)₂ MOF film. The Cu thin film was both the substrate and the Cu source in this method. This heteroepitaxial growth process allowed the MOF thin film to grow uniformly on the surface of the substrate, yielding both high crystallinity and a large specific surface area that can reach 723 m²/g. Another obvious advantage of this preparation method is that the film can maintain a strong bonding force with the substrate, which provides feasibility for the subsequent processing of the film. The heteroepitaxial growth method proposed in this work to prepare MOF films provides a potential means for increasing the utilization of MOF materials in more planar electronic devices.

In 2022, Kisan Chhetri et al. used bimetallic MOFs and HCNFs to synthesize electrode materials (Figure 8).¹⁴⁰ At first, they prepared the HCNFs from the core-shell electrospinning technique, followed by successive stabilization and carbonization. The bimetallic MOFs (Ni and Fe based) were synthesized inside and outside of the HCNFs and converted into bimetallic phosphide (Ni-Fe-P) via phosphidization. The HCNFs with the inside-outside grown bimetallic phosphide nanostructures have shown reduced ion/electron transport pathways and enhanced Faradic reactions on electrode/electrolyte interfaces to increase overall electrochemical performance as an electrode material for supercapacitors. In addition, MOFs derived from bimetallic phosphide nanostructures inside and outside the HCNFs with a unique design, porosity, and hollow channel can improve the kinetics of charge transfer by establishing three different layers, i.e., (MOF-Substrate-MOF)-derived from bimetallic phosphide at HCNFs. Also, inside and outside decoration of bimetallic phosphide at the HCNFs avoided the overlapping of carbon materials during the cycling test by preventing π - π interaction and providing enhanced electrochemical performance. Such (MOF-Substrate-MOF)-derived from bimetallic phosphide at HCNFs with enhanced electrochemical performance is the novelty of this work. The as-prepared (Ni-Fe)-PC@HCNFs was used as a positive electrode, and Fe-P-C@HCNFs was used as a negative electrode to fabricate the asymmetric supercapacitor device. The authors explored the potential of MOFs decorated HCNFs derived bimetallic phosphide-based electrode materials as the alternative option for the development of efficient electrode material for energy storage applications. The synthesized material's excellent electrochemical performance was owing to the co-existence of numerous Ni and Fe-based redox-active species with porous carbon and open channels from MOF-derived Carbon at HCNFs for fast electrolyte ions/electron diffusion. Consequently, the (Ni-Fe)-P-C@HCNFs electrode had a high specific capacitance of 1392 F/g at 1 A/g and good cycling stability, with capacitance retention of approximately 89% at 25 A/g. Moreover, after 10,000 cycles, the asymmetric supercapacitor (ASC): (Ni-Fe)-PC@HCNFs//Fe-P-C@HCNFs revealed an optimal energy density of 62.7 Wh/kg and a power density of 8238.2 W/kg, with cycling stability of 92.4 percent at a high current density of 25 A/g.

Porous polymers electrodes

Porous polymers refer to a polymer material with a permanent and definable porosity and are a new and popular multifunctional material. Porous polymers are constructed by rational chemical synthetic design and thus can achieve controllable pore structures and sizes. In addition, this type of polymer material also possesses high processing performance due to its facile dispersion (or even dissolution in some solvents) and can be directly prepared into thin films or bulk materials, making it very suitable for many practical applications. Furthermore, the diversity of synthetic routes for chemical materials enables the construction of polymers that can incorporate a variety of chemical functional groups into porous frameworks or pore surfaces. This provides a direct route to the manipulation of chemical or physical properties to meet the needs of various applications, making porous polymers a highly diverse field that has attracted attention of researchers in recent years.¹⁴¹⁻¹⁴⁵

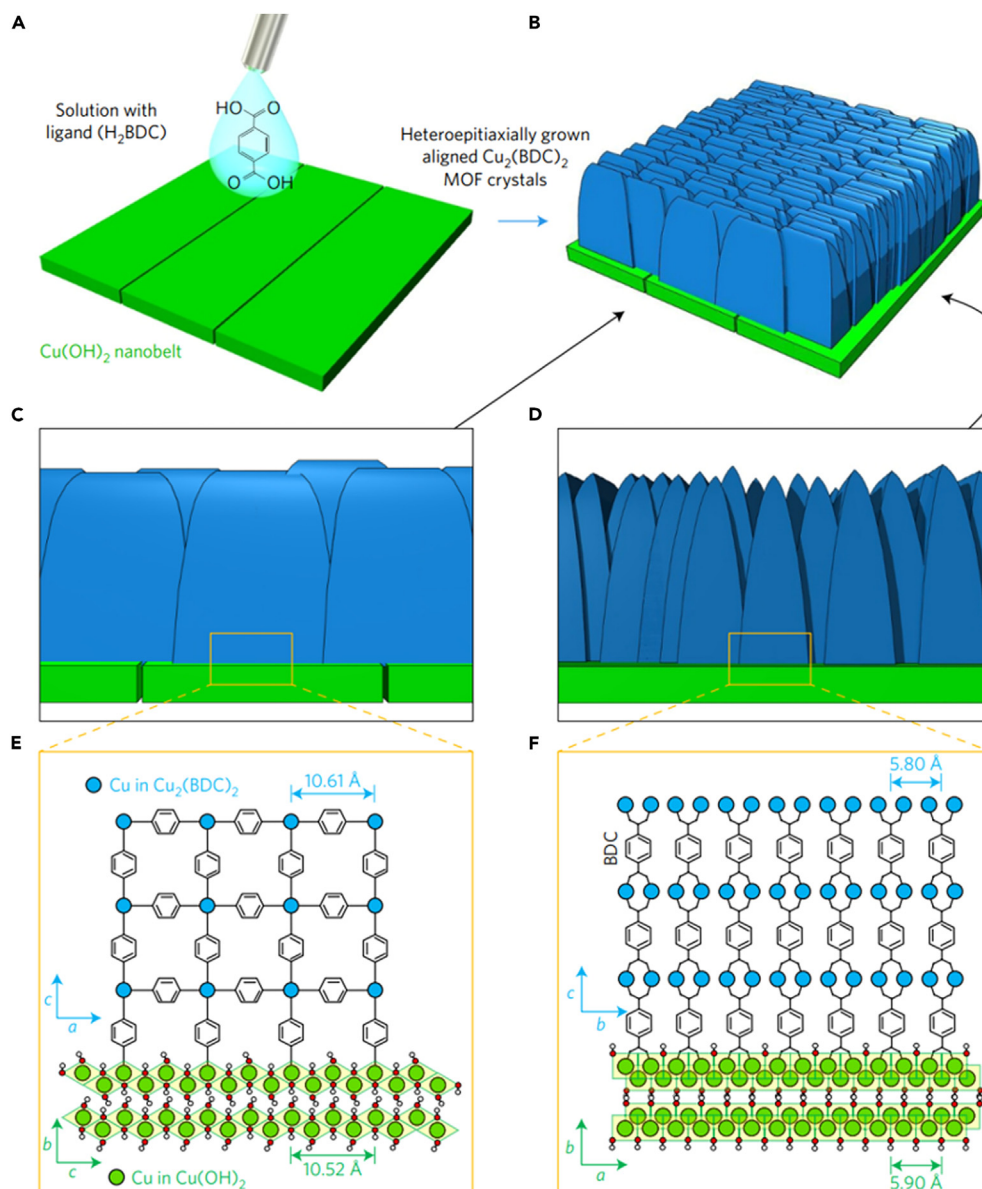


Figure 7. Approach to fully oriented MOF growth

Heteroepitaxial growth of $\text{Cu}_2(\text{BDC})_2$ MOFs on single-crystal $\text{Cu}(\text{OH})_2$ nanomaterials.

(A) Ligand (H_2BDC)-containing solution is placed in contact with the $\text{Cu}(\text{OH})_2$ nanobelt (green plate).

(B) $\text{Cu}_2(\text{BDC})_2$ MOFs (light blue triangles) are heteroepitaxially grown on the $\text{Cu}(\text{OH})_2$ nanobelt.

(C, D) Magnified image of the interface of $\text{Cu}_2(\text{BDC})_2$ MOFs and $\text{Cu}(\text{OH})_2$ along parallel and perpendicular directions to the long axis of $\text{Cu}(\text{OH})_2$ nanobelts.

(E, F) Crystal structures of both $\text{Cu}(\text{OH})_2$ and $\text{Cu}_2(\text{BDC})_2$ MOFs are schematically shown. Reproduced with permission from ref. ¹³⁹ Copyright 2016 Nature.

Porous polymers can be divided into classes based on their pore sizes: microporous materials (<2 nm pores), mesoporous materials (2 nm–50 nm pores), and macroporous materials (>50 nm pores). The microporous structure is the most effective at increasing the specific surface of the material, but the very small pore size also limits the accessible void space and diffusion paths, hindering the effective use of the surface area to some extent. This is overcome in the mesoporous structures, which provide less theoretical surface area than microporous materials but do allow better diffusion and surface area exposure. Polymers with “microporous-mesoporous” hierarchical pore structure can combine the advantages of both micropores and mesopores, and are an important hybrid class of porous polymer materials.

Porous polymers are generally bonded by stable covalent bonds and can be divided into hypercrosslinked polymers (HCPs), polymers of intrinsic microporosity (PIMs), covalent organic frameworks (COFs), conjugated microporous polymers (CMPs), and coordination porous polymers (CPP).

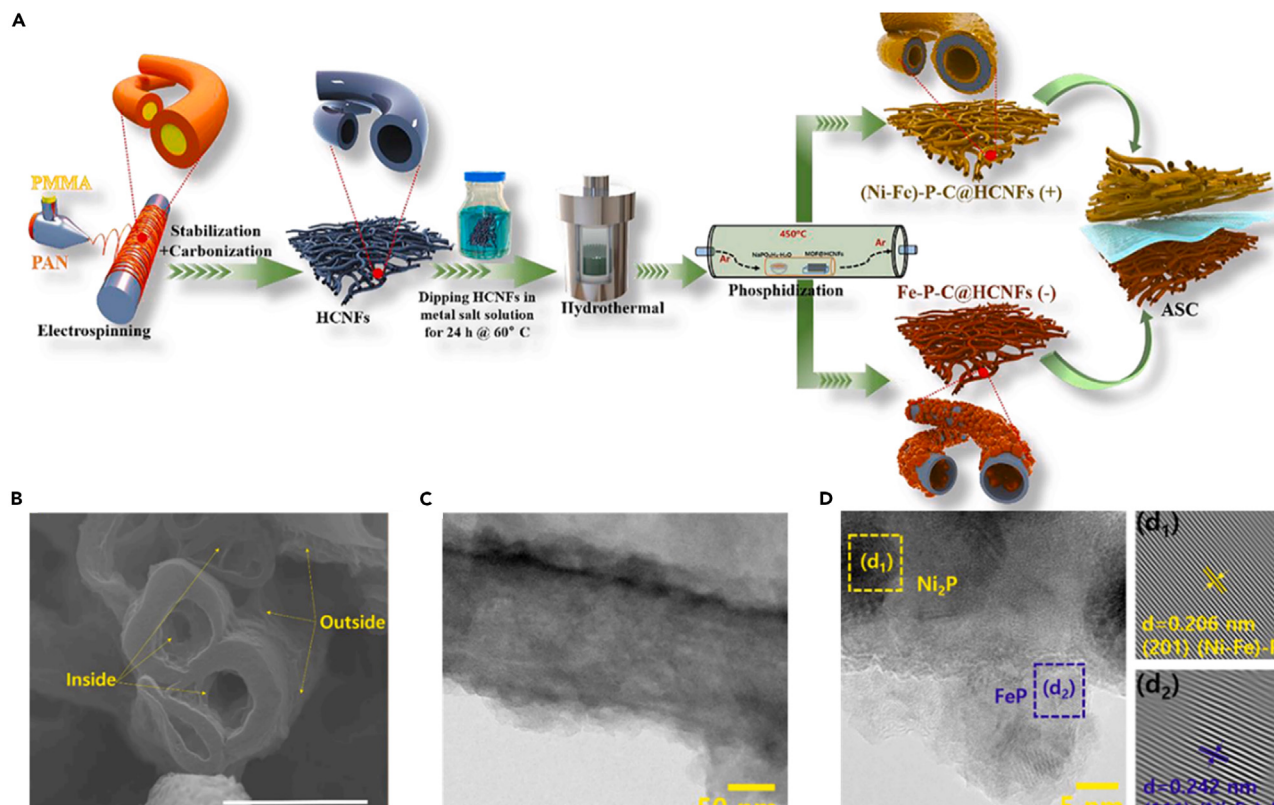


Figure 8. Synthesis and surface characterizations of (Ni-Fe)-P-C@HCNFs

(A) Synthesis route for (Ni-Fe)-P-C@HCNFs electrode materials preparation.

(B–D) TEM, HR-TEM images of (Ni-Fe)-P-C@HCNFs. Reproduced with permission from ref. ¹⁴⁰ Copyright 2022 Chemical Engineering Journal.

Conjugated microporous polymers (CMPs) are materials with large π -conjugated systems composed of aromatic systems or unsaturated carbon-carbon bonds. This material effectively combines the conjugated and porous properties of some polymer materials and can exhibit unique optoelectronic properties. CMPs have been the focus of extensive research and can be used toward important applications in the field of energy storage and conversion.

In 2011, Jiang et al. reported the application of CMPs as electrode materials for MSCs. Using 1,2,4,5-phenylenetetramine and cyclohexanone as monomers, they prepared a series of aza-fused conjugated microporous polymers (Aza-CMPs) through condensation reactions at different temperatures. The specific surface area of Aza-CMPs can reach up to $1,227 \text{ m}^2/\text{g}$.¹⁴⁶ The electrode film can be prepared by grinding and mixing the Aza-CMP powder, a conductive assistant (acetylene black), and a binder such as polytetrafluoroethylene. In the three-electrode system, with 1 M H_2SO_4 solution as the electrolyte, the measured capacity of this material can reach up to 818 F/g, and the energy density can reach 53 Wh/kg. Notably, this material exhibited ultrahigh cycling stability as a supercapacitor electrode material, with no capacity loss after 10,000 charge-discharge cycles at a current density of 5 A/g. The excellent capacitive performance of Aza-CMPs can be attributed to (1) the fused, conductive nature of the frameworks; (2) the capability of the aza units to generate dipole interactions with cations or protons in the electrolyte that can store charge by accumulation on the internal surface; (3) the optimized porous structure that can achieve the rapid transport of ions during the charging and discharging process; and (4) the high specific surface area, which can separate the electrostatic charges formed in the pores and provide more interface space. This work opens up new ideas for the application of CMPs in energy storage fields such as supercapacitors.

Composite electrodes

In addition to the above single-component electrode materials, some multi-component composite materials or composite structures can integrate components that offer benefits to each other, combining the advantages of multiple materials. Therefore, there are also many studies on the preparation and design of new composite electrode materials, which can be effectively used in electrochemical energy storage devices to further improve their performance.¹⁴⁷ In the field of planar MSCs, there have been many works aimed at studying composite electrodes; among them, there are composites based on pure carbon, hybrids of carbon and some pseudocapacitive materials, and other meta-form and related structural composites. However, when multiple components are compounded, they sometimes demonstrate incompatibility, and the final composite material can be prone to the shortcomings of component agglomeration and reduced film-forming properties, decreasing their effectiveness in MSCs.

In 2012, Wang et al. prepared pure carbon composites based on graphene and CNTs and fabricated them into planar MSCs.¹⁴⁸ First, the reduced graphene (as rGO) and CNT precursor solutions were mixed in a certain proportion to prepare slurry, followed by deposition on a preheated gold interdigitated electrode by electrostatic spray deposition. An aqueous potassium chloride solution was used as the electrolyte to obtain a micro-capacitor. This type of composite material features CNTs interspersed between graphene sheets, effectively weakening the “re-stacking” effect of graphene, increasing the specific surface area of the composite material, and generating more internal space to facilitate the infiltration of electrolytes. Therefore, compared with MSCs using single reduced graphene as the electrode material, the capacitive performance of the hybrid graphene-CNT composites has been significantly improved.

The effective combination of highly conductive graphene and high-performance pseudocapacitive materials is the most common preparation form of composite electrode materials. In 2013, Yu et al. prepared planar MSCs with MnO₂ nanosheets/graphene hybrid materials as electrodes.¹⁴⁹ MnO₂ nanosheets were prepared by an oxidation exfoliation method, and graphene was prepared by reducing graphene oxide with hydrazine hydrate; negatively charged manganese oxide and positively charged graphene were combined and electrostatically attracted to each other. The surface possessed abundant redox active sites and created additional space between graphene layers to facilitate fast charge transport. Compared to MSCs with pure graphene as the electrode, which exhibited a capacity of about 140 F/g, the capacity of the MnO₂/graphene composite as the electrode can reach about 254 F/g. Further, when the density was increased from 0.5 A/g to 10 A/g, the capacity loss of the MnO₂/graphene micro-capacitor was only about 22%, which is better than the 56% capacity loss of the pure graphene MSC.

In 2016, Feng et al. prepared planar micro-capacitors based on MXene/electro-exfoliated graphene composites (MXene@EG) (Figures 9A and 9B).¹⁵⁰ After mixing the MXene (prepared by an ultrasonic-assisted acid etching method) and the graphene (prepared by an electrochemical exfoliation method) into slurry, it was spray-deposited upon a mask with an interdigitated structure onto the surface of the PET substrate and dried to obtain a flexible micro-capacitor. The micro-capacitor showed good electrochemical performance, with an area capacitance (C_A) reaching 3.26 mF/cm² and a volume capacitance (C_V) of 33 F/cm³; it simultaneously exhibited excellent flexibility characteristics and it could be used during bending and straightening. After 2500 charge-discharge cycles, the capacity was maintained at around 82%. In addition, reduced graphene and MoS₂ nanosheet hybrid materials have also been used for the fabrication of planar MSCs.¹⁵¹

The above works are based on graphene/metal compound composites. In addition, graphene and some high molecular polymers can also be prepared into composite electrodes by various methods. In 2016, Wu et al. prepared a hybrid material with a stacked heterostructure (Figures 9C–9G), which was composed of stacking thiophene (TP) nanosheets and electro-exfoliated graphene (EG) layer by layer.⁷³ The TP nanosheets were self-assembled from copolymers containing the thiophene functional group. The thickness of a single sheet was about 3.5 nm and demonstrated excellent pseudocapacitive properties. The TP/EG composites, with a total thickness of about 105 nm, exhibited large-area uniformity and can be directly transferred onto PET substrates as a binder- and additive-free flexible electrode. Finally, the C_A of the micro-capacitor with PVA/H₂SO₄ as electrolyte can reach up to 3.42 mF/cm², and the C_V can reach up to 326 F/cm³. Benefiting from the efficient charge diffusion and transfer rate brought by the TP/EG heterostructure, the equivalent series resistance (ESR) of the micro-capacitor was only 2.4 Ω , and the RC time constant (τ_0) is 1.2 ms. In addition, in the case of 180° bending, the TP/EG micro-capacitor still maintained 97% of the original capacity, showing its excellent flexibility.

In 2015, Wong et al. reported a micro-capacitor using graphene/polyaniline (PANI) composite as electrode material (Figures 10A–10F).¹⁵² They dispersed reduced graphene and PANI in water to make slurry, which was then spin-coated on the surface of a polyimide substrate to obtain an electrode film. After deposition of a gold current collector on the film and subsequent etching, PVA/H₂SO₄ was used as the electrolyte, and a planar micro-capacitor (rG/SP-MSC) is finally obtained. rG/SP-MSC had good electrochemical performance; the area capacitance (C_A) reached 3.31 mF/cm² at a scan rate of 10 mV/s, and at an increased rate of 2000 mV/s, this capacitance was still able to reach 2.03 mF/cm². Further, the capacity retention was 97.5% after 1,000 cycles in the flexed position and 96.5% after 1,000 more cycles in the twisted position, showing good cycling stability despite mechanical deformation of this type of device. Similarly, Wang et al. also reported an interdigital MSC with polypyrrole (PPy)/carbon composite microstructure as electrodes.¹⁴⁷

In addition to the combination of two materials, there are also many important works using three or more substances to prepare composite active electrodes for planar micro-capacitors, in order to derive even more benefits from constituent materials. This strategy holds much promise in the development of active electrodes for energy devices. Tay et al. combined reduced graphene (rGO), acicular (needle-like) manganese dioxide (MnO₂), and silver nanowires (AgNW), and prepared a very uniform film by vacuum filtration. After transfer, etching and other processing steps, the final result was a composite planar micro-capacitor.¹⁵⁴ Using an ionic liquid as the electrolyte, the energy density of this micro-capacitor can reach 2.3 mWh/cm³ when the power density was 162.0 mW/cm³. In addition, its resistance-capacitance time constant was only 0.16 ms, which is better than some pure carbon materials.

In 2016, Zhang et al. prepared a CNT/activated carbon/MnO₂-based hybrid electrode micro-capacitor (Figures 10G–10I).¹⁵³ A layer of CNT was first grown on the surface of the substrate, then photolithography was used to generate an interdigitated structure, followed by carbonization at high temperature to form a carbon material layer, and final electrodeposition of MnO₂ nanosheets to obtain a three-layer hybrid material. The micro-capacitor had an area capacitance (C_A) of 0.55 mF/cm² and a volumetric capacitance (C_V) of 20.4 F/cm³; the capacity retained 92.4% after 5,000 charge-discharge cycles.

Covalent organic frameworks (COFs) are an emerging class of porous polymer due to their well-defined channels, highly accessible surface areas and tunable active sites. However, their low inherent conductivity and poor accessibility (difficult to dissolve or melt) have largely limited their electrochemical performances and practical applications. To solve this problem, Ning An et al., just in this year (2023), introduced

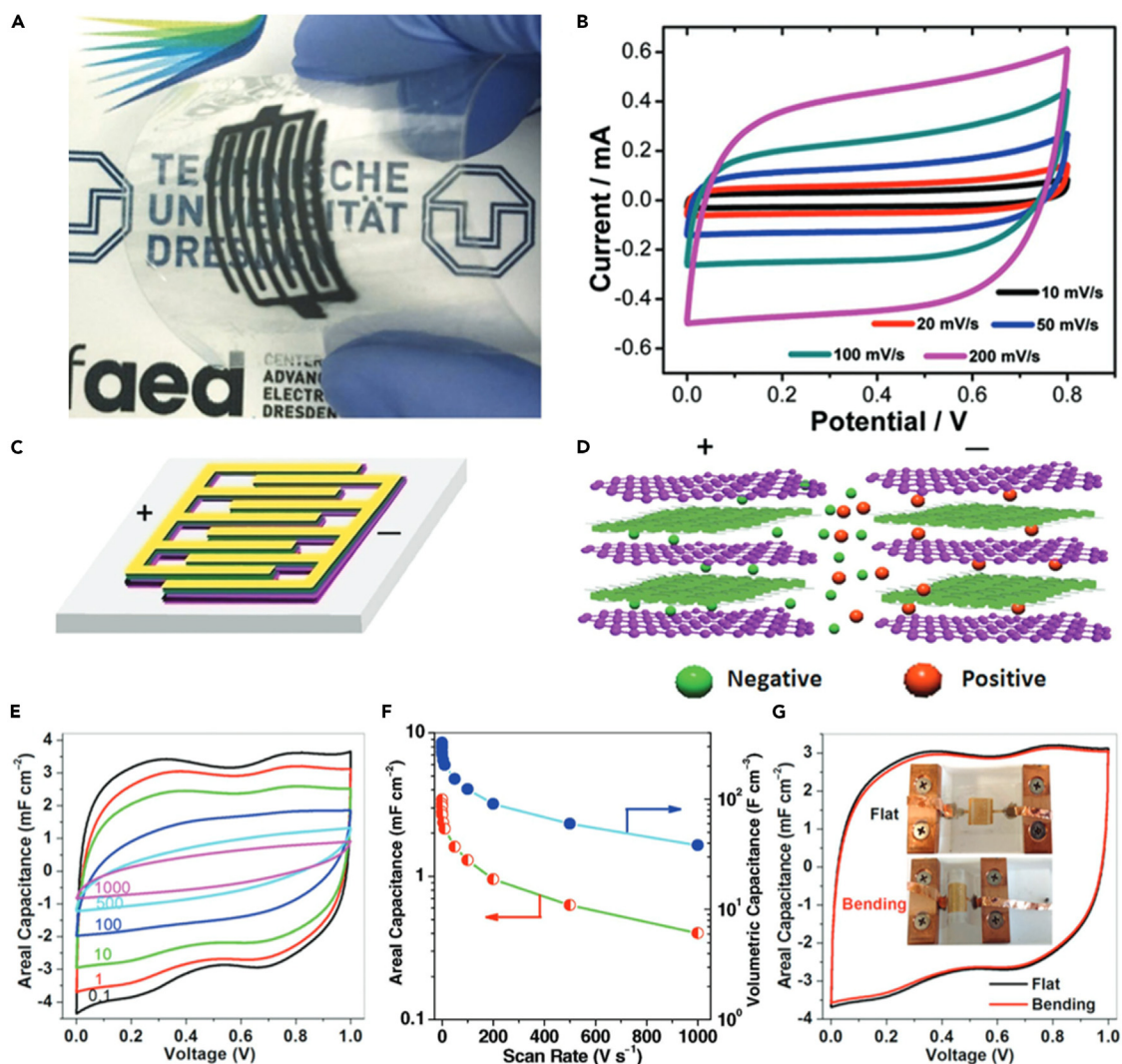


Figure 9. MSCs based on MXene/exfoliated graphene hybrid materials and their performance

(A) Photograph of the flexible in-plane MSC based on EGMX1:3 hybrid ink on a PET substrate.

(B) CV curves of MSC based on EGMX1:3 at different scan rates of 10, 20, 50, 100, and 200 mV/s. Reproduced with permission from ref.¹⁵⁰ Copyright 2016 WILEY-VCH.

(C–G) MSCs based on thiophene nanosheets/graphene hybrid materials. Scheme of (C) the planar TP/EG-MSCs in top view and (D) side view of charging state, respectively. (E) CV curves of TP/EG-MSCs obtained at different scan rates from 0.1 to 1000 V/s. (F) The areal capacitance and volumetric capacitance of TP/EG-MSCs as a function of scan rate. (G) CV curves of TP/EG-MSCs obtained at 1 V/s under flat and bending state. Inset: the photographs of the TP/EG-MSCs under flat and bending states. Reproduced with permission from ref.⁷³ Copyright 2016 WILEY-VCH.

MXene(transition metal-based electrodes) to prepare composite electrodes materials (Figure 11)¹⁵⁵ They selected anthraquinone-based COFs (DAAQ-COFs) as active material and layered $Ti_3C_2T_x$ MXene as flexible conductive substrate to construct DAAQ-COFs/MXene flexible film electrode (CMF). The uniform intercalation of porous COFs in layered MXene was realized by electrostatic attraction between negatively charged 2D MXene nanosheets and the protonated DAAQ-COFs. Porous COFs tightly contacting with MXene, resulting in CMFs film, effectively alleviate the self-restacking of MXene nanosheets. Benefits from abundant and ordered one-dimensional pore structure of COFs and excellent intrinsic 3D conductive network of MXene, the electrode achieves rapid electron transfer, ion migration and reaction kinetics. In the three-electrode system, the integrated CMFs film electrode delivers excellent electrochemical performances (the capacitance of 390 F/g at 0.5 A/g), excellent kinetic energy storage characteristics (capacitive contribution can be up to 96.7% at 50 mV/s) and superb mechanical strength (repeated bending 100 times). By assembling into all-solid-state flexible supercapacitor, CMFs//CCMP asymmetric supercapacitors (ASC) achieves the maximum energy density of 27.5 Wh/kg (at a power density of 350 W/kg), maximum power density of 7000 W/kg (at an energy density of 19.7 Wh/kg) and the ultrahigh capacitance retention of 88.9% after 20,000 charging-discharging long cycles, suggesting great potentials for the applications in future flexible and wearable devices.

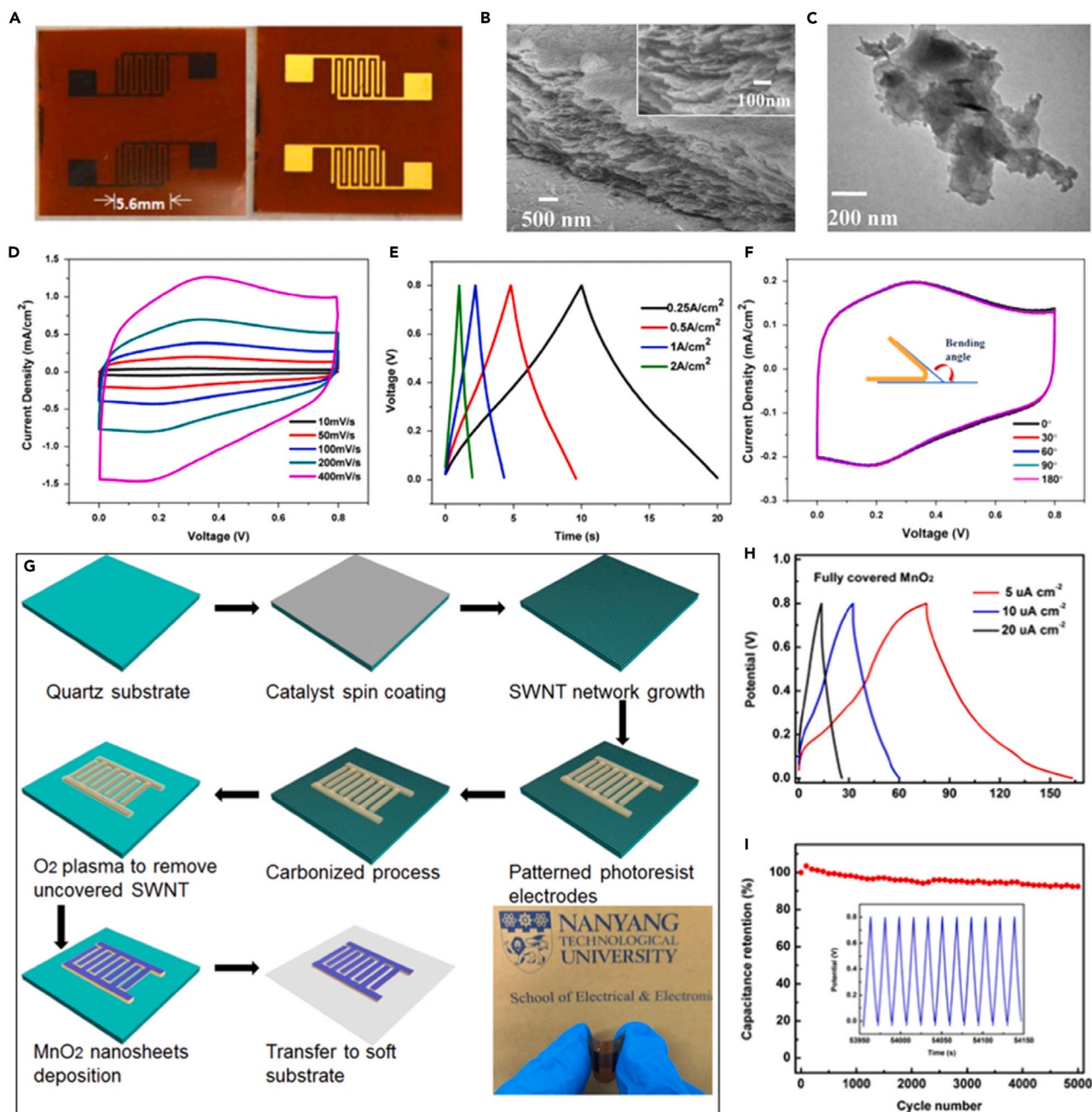


Figure 10. Flexible MCSs based on graphene/PANI composites and their performance

(A) Digital image of the back side (left) and front side (right) of the as-fabricated rG/SP-MSC.

(B) Cross-section SEM images of the deposited rG/SP microelectrodes on Kapton substrate with a magnified image in the inset.

(C) TEM image of the rG/SP composite.

(D) CV profiles at different rates of 10–400 mV/s.

(E) Galvanostatic charge/discharge curves at current densities from 0.25 A/cm² to 2 A/cm².

(F) CV performance of the device with different bending angles tested at 50 mV/s. Reproduced with permission from ref.¹⁵² Copyright 2015 Elsevier.

(G–I) MSCs based on SWNT/carbon/MnO₂ hybrid electrode. (G) Fabrication flow charts and photo of the designed MSC on a soft substrate.

(H) The GV curves of fully covered electrode tested at 5, 10 and 20 μA/cm². (I) Specific capacitance of the solid MSC with SWNT/carbon/MnO₂ electrodes as a function of cycle number. Reproduced with permission from ref.¹⁵³ Copyright 2016 Elsevier.

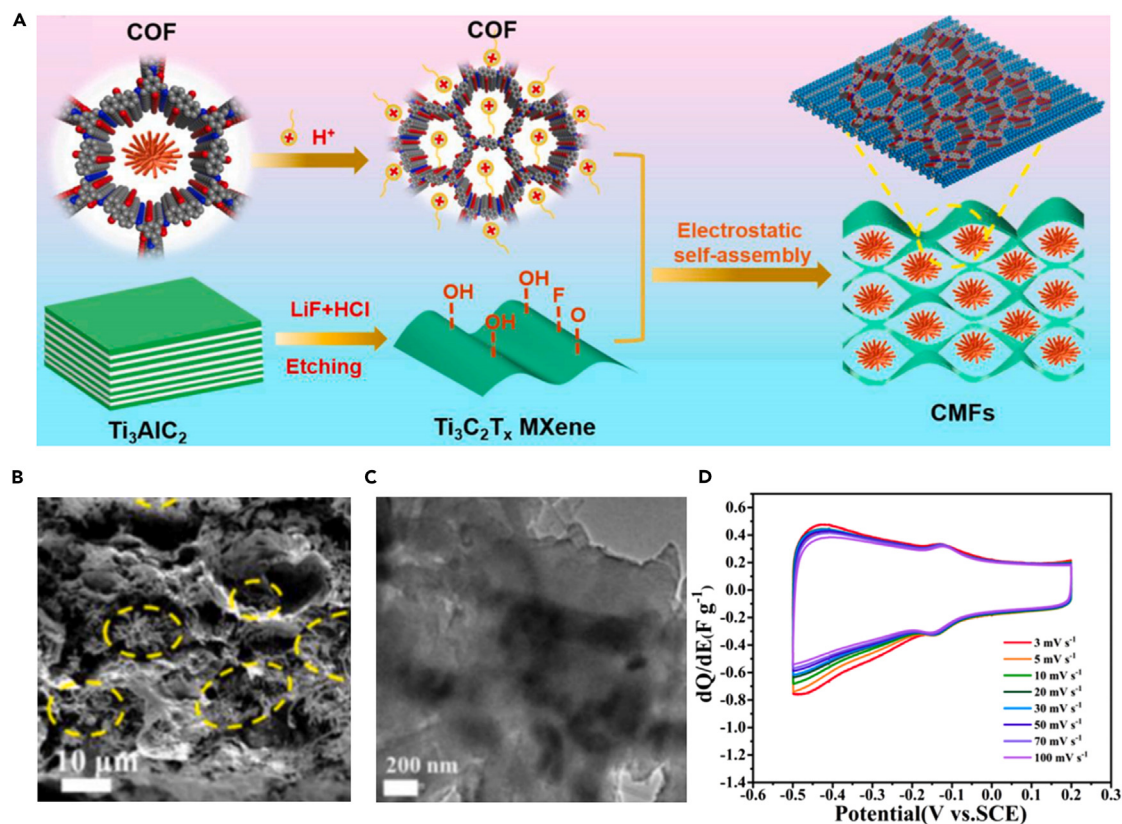


Figure 11. CMFs preparation and performance

(A) Schematic of CMFs preparation.

(B) Cross-sectional SEM images of the CMFs.

(C) TEM images of CMFs.

(D) Capacity vs. potential curves at different scan rates of CMFs electrode material. Reproduced with permission from ref.¹⁵⁵ Copyright 2023 Chemical Engineering Journal.

The preparation of composite electrodes is an effective method to make planar micro-capacitors that have both high energy and power density, and the work of many researchers has made outstanding achievements in this regard. However, methods to combine multi-materials more effectively, to reach the full potential of the advantages of their respective components, and to prepare electrode films more simply and robustly is still an important challenge for researchers in this field.

SUMMARY AND PERSPECTIVES

In summary, we have discussed the characteristics of the different electrode materials for MSCs, and electrochemical performance of several representative materials are compared in Table 2. Besides, the advantages and disadvantages of different types of electrode materials are summarized in Figure 12. Carbon-based materials are among the most widely used electrode materials and have been commercially applied. Moreover, MSCs based on carbon-based materials can exhibit excellent mechanical stability and have great potential for wearable flexible electronic systems. MSCs based on transition metal-based electrode materials have great advantages on the energy density. However, to improve the cycle stability, carbon-based materials and conductive polymers are generally introduced, which leads to complex preparation processes and limits their application in MSCs. MSCs based on conductive polymers have high energy storage density, good mechanical flexibility, easy synthesis (mostly prepared into electrode films by electrodeposition) and low cost, so they have great potential for practical applications in MSCs. CPFs as a new type of “organic-inorganic” hybrid functional materials have aroused strong interest of researchers, and with the increasing efforts in this area, more and more favorable properties are being discovered and developed, which provides more potential means for increasing the utilization of CPFs in more planar electronic devices. Porous polymers are a new and popular multifunctional material. This material possesses high processing performance due to its facile dispersion (or even dissolution in some solvents) and can be directly prepared into thin films or bulk materials, making it very suitable for many practical applications. Composite electrodes help combine the advantages of multiple materials with both high energy density and high power density, which is an important trend in the development of nanostructured electrode materials for MSCs.

However, the electrochemical performance of MSCs still faces huge challenges.^{158,159} The most prominent disadvantage of MSCs is insufficient energy density.¹⁶⁰ The key to improving electrochemical performance of MSCs, including energy density and power density, is to

Table 2. Comparison of electrochemical performance of representative nanostructured electrode materials for MSCs

Electrode materials		C_A ($\mu\text{F}/\text{cm}^2$)	C_v (F/cm^3)	Energy density (mWh/cm^3)	Power density (W/cm^3)	Capacitance retention (%)	Cycle stability	Reference
Carbon	rGO	80.7	17.9	2.5	495	98.3	100,000	Wu et al., 2013 ⁷⁹
	SG	553	582	3.1	1,191	95.0	10,000	Wu et al., 2017 ⁸⁰
	MWCNT	–	5.0	0.4	0.19	98	10,000	Kim et al., 2014 ⁸⁴
	SWNT@C	37.1	48.5	3.7	0.0457	98.5	10,000	Meng et al., 2014 ¹⁵⁶
	AC	0.9	9.0	10	1,000	–	10,000	Pech et al., 2010 ⁸⁸
Transition metal	MnO _x /Au	–	32.8	1.75	3.44	74.1	15,000	Si et al., 2013 ¹¹⁴
	Ti ₃ C ₂ T _x	27,300	356.8	11–18	0.7–15	100	10,000	Peng et al., 2016 ¹⁰⁰
	MoS ₂	8,000	180	–	–	92	1000	Cao et al., 2013 ¹¹⁵
	VS ₂	4,760	317	–	–	90	1000	Feng et al., 2011 ¹⁵⁷
Conductive polymer	PANI	45,200	105	7.4	128	93.1	2000	Meng et al., 2014 ¹²⁶
	Ppy	420,000	11	1.0	0.27	75.6	10,000	Yuan et al., 2013 ¹²⁷
Coordination polymer frameworks	PiCBA	150	34.1	4.7	1323	86	350	Yang et al., 2017 ¹³³
	MOF	5,085	0.64	0.286	0.386	80	10,000	Choi et al., 2014 ¹³⁴
Porous polymers	Aza-CMP	818 F/g		53 Wh/kg	–	–	10,000	Kou et al., 2011 ¹⁴⁶
Composite	MXene@EG	3,260	33	1.4	1.6	82	2500	Li et al., 2017 ¹⁵⁰
	TP@EG	3,420	326	13	776	86	10,000	Wu et al., 2017 ⁷³
	rG@SP	3,310	16.55	1.51	–	97.5	1000	Song et al., 2015 ¹⁵²
	SWNT@C@MnO ₂	550	20.4	–	–	92.4	5000	Sun et al., 2016 ¹⁵³

explore new and optimize existing electrode active materials. The preparation of composite and hybrid electrode materials is also an effective method, and much work has also made outstanding research results in this regard.¹⁵⁵ How to combine multiple materials most effectively to maximize the advantages of their respective components and to integrate them into MSCs will be an important field of research in the future.

Besides, great efforts are still required to promote commercialization in various aspects.^{161,162} First, as an energy storage device, MSCs play an important role in ensuring the long-term continuous and stable operation in the microelectronic devices.¹⁶¹ Hence, the cycle stability is an important aspect when designing devices. Second, considering the practical application scenarios such as smart phones, implantable medical devices, and microsensors, the environmental factors including temperature, humidity and pH conditions also need to be resolved.¹⁶³ Third, developing cost-effective and high-resolution microfabrication techniques is significant for scalable production of miniaturized MSCs. Although many electrode material fabrication technologies have been developed for MSCs, such as lithography, CVD and inkjet printing, each method has its own limitations waiting to be conquered. The mass-scale industrial production by these methods is restricted by low fabrication efficiency and high cost.¹⁶⁴ Therefore, microfabrication methods compatible with various electrode materials is crucial to promote and realize the industrial mass production of MSCs. Fourth, the electrochemical performance such as areal energy of MSCs is not only restricted by electrode materials, 3D structure design of electrode is also necessary. The thickness of microelectrodes is usually extremely restricted by the above microfabrication technology, resulting in limited mass loading of active materials. To optimize the device architectures, developing thick electrodes with high mechanical strength based on 3D porous current collector with high electron-ion transport channels, decreasing the content of inactive materials or increasing the space utilization by reducing inter-electrode spacing and designing fractal electrode configuration are effective strategies. Finally, miniaturization, mechanical properties, flexibility, biocompatibility, and biodegradability¹⁶⁵ are also important considerations for integration with microelectronic systems. In fact, it is difficult to combine MSCs with microelectronic system due to their relatively independent development. Generally, laboratory research focuses on optimizing the performance of devices, regardless of their application in integrated circuit and microelectronic systems, leading to inevitably incompatible and mismatched problems. Therefore, the cooperation of electrical engineers and researchers in MSCs toward practical application is very necessary.

ACKNOWLEDGMENTS

This work is supported by the National Key Research and Development Project (2018YFE0124800), the National Natural Science Foundation of China (51702157).

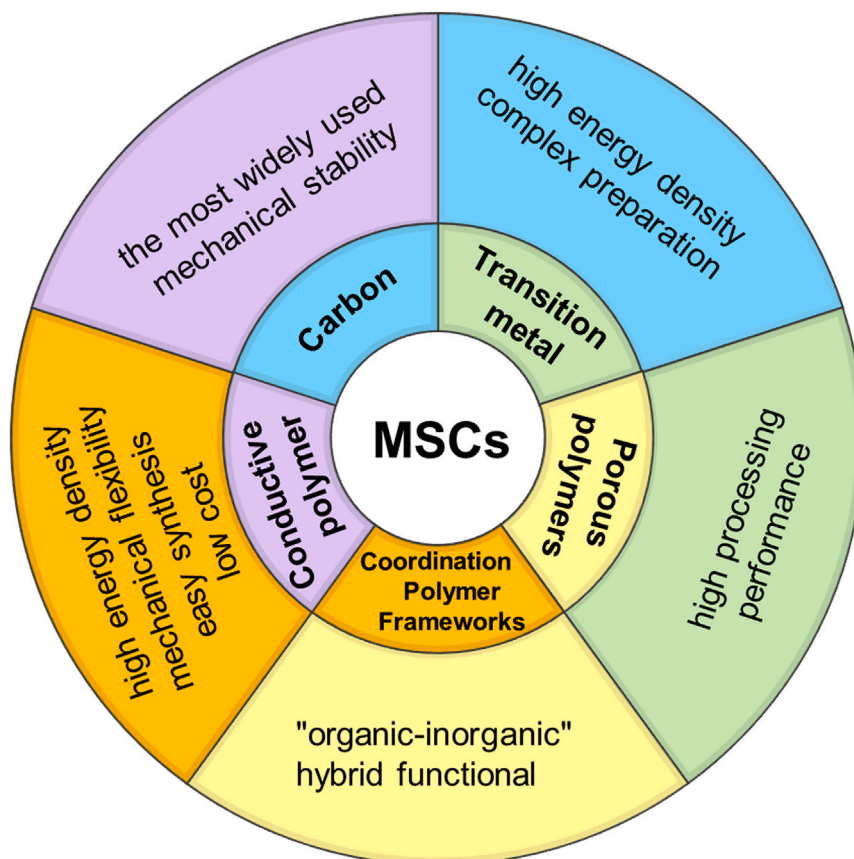


Figure 12. Comparison of the advantages and disadvantages of different types of electrode materials

AUTHOR CONTRIBUTIONS

Y.X.: Writing—original draft preparation; S.Y.: Conceptualization; H.M.J.: Validation; Y.W.: Investigation; X.L.: Resources; B.F.: Writing—review and editing; Y.Z.: Supervision; All authors have read and agreed to the published version of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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