Emerging smart design of electrodes for micro-supercapacitors: A review

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Abstract
Owing to high power density and long cycle life, micro-supercapacitors (MSCs) are regarded as a prevalent energy storage unit for miniaturized electronics in modern life. A major bottleneck is achieving enhanced energy density without sacrificing both power density and cycle life. To this end, designing electrodes in a “smart” way has emerged as an effective strategy to achieve a trade-off between the energy and power densities of MSCs. In the past few years, considerable research efforts have been devoted to exploring new electrode materials for high capacitance, but designing clever configurations for electrodes has rarely been investigated from a structural point of view, which is also important for MSCs within a limited footprint area, in particular. This review article categorizes and arranges these “smart” design strategies of electrodes into three design concepts: layer-by-layer, scaffold-assisted and rolling origami. The corresponding strengths and challenges are comprehensively summarized, and the potential solutions to resolve these challenges are pointed out. Finally, the smart design principle of the electrodes of MSCs and key perspectives for future research in this field are outlined.

KEYWORDS
energy density, layer-by-layer, micro-supercapacitors, rolling origami, scaffold, smart design of electrodes

1 | INTRODUCTION

Heretofore, microelectronic devices have dramatically facilitated the quality of modern life than before thanks to evolving in leaps and bounds in recent years of advanced microfabrication technologies. Many novel electronic products have been developed, such as wearable electronics, portable devices, health monitoring systems, intelligent tiny robots, implantable medical components, biomedical sensors, radio frequency identification tags, and wireless network system devices in the Internet of Things (IoT), and these products have pervaded into areas that we are living in and profoundly changed our lifestyle. Although some of these electronic devices can power themselves via harvesting and converting renewable energy (e.g., solar, wind, and geothermal energy) into electricity, due to the certain intermittence or randomness of these renewable sources, an energy storage unit is still needed as an energy buffer to ensure the continuous power supply for the whole network.1,2 To be compatible with the miniaturized electronic devices, the energy storage unit should be small enough to...
be assembled and/or embedded directly into circuit boards. Among various types of energy storage devices, microbatteries (MBs) and micro-supercapacitors (MSCs) have been investigated intensively over the past decades as complementary energy supplement systems to satisfy the ever-increasing requirement of self-powered miniaturized network devices.2–4 MBs have been successful to some extent as an energy source, but still suffer from generic power density and limited cycle life.5 The energy density of MSCs is mediocre compared with MBs, but still enable to power long-range communication devices for hours, such as GPRS, 3G, 4G, and so forth, as depicted in Figure 1.6,7 At the same time, owing to high power density (>10 mW/cm²) and excellent cycle life (>100,000 cycles), MSCs have been considered as one of the most promising complements or alternatives for MBs.8,9 Charge storage mechanisms involved in MSCs are the same as those of conventional bulk supercapacitors.10,11 To meet the requirements of practical microelectronic applications, considerable research efforts have been devoted to enhancing the energy storage capability of MSCs. At present, the bottlenecks encountered by MSCs are to realize enhanced energy density without sacrificing both power density and cycle life. Possible solutions can be divided into two parts: the exploration of new active materials and the optimal design of electrode architecture for assembling these materials with appropriate dimensions.12 It is worth noting that, in contrast to conventional bulk supercapacitors, MSCs pursue a higher utilization ratio per footprint area, for which it also put forward much higher requirements on the electrode structure design and corresponding fabrication techniques. So far, quite a few “smart” designs of electrodes have emerged toward improving the energy storage capability of MSCs. In this review, “smart design of electrodes” is defined as the strategies for rational structure configuration of electrodes to make full use of the limited space for higher energy storage capability of MSCs. These designed electrodes generally possess unique topologies of the electrode structure and sufficient utilization of active materials, thereby improving areal energy storage and transportation performance within a small footprint to meet the requirements of practical applications. This review aims to highlight these “smart” design strategies of electrodes, summarize their corresponding advantages and challenges, thereby outlining potential solutions to these challenges and key perspectives of future research in this field.

2 | SMART DESIGN CONCEPTS OF ELECTRODES AND THEIR ADVANTAGES

To be compatible with miniaturized wireless network devices like smart sensors, supercapacitors are miniaturized into micros as MSCs, covering a footprint area close to several square millimeters. Moreover, further scaling down the size of the device is required so as to be used as micro/nano intravascular implants for healthcare and medical treatment. It is important to keep in mind that high power and energy densities have always been the scientific pursuits for MSCs as alternatives for MBs. However, the scaling down of device size inevitably leads to compromise of the mass loading of electrode active material per unit area of MSCs, which directly lowers the energy storage capabilities.8,9 Accordingly, the main challenge for MSCs is to maximize the energy density without sacrificing power density and lifespan within several square millimeters. Like supercapacitors, the energy performance of MSCs is defined as \( E = CV^2/2 \). And perfect MSC always is the science pursue which possesses the advantages listed: (i) high areal capacitance; (ii) high areal energy density; (iii) high areal power density; (iv) good cycle retention; and (v) enough volumetric energy density. As known, current collectors, electrochemical active materials, and its mass loading are the three major factors that affect the capacity of supercapacitors, while the optimal electrolyte and asymmetric device configuration are the main pathways to obtain a higher potential window. In recent years, research has focused on exploring advanced electrode materials and electrolytes for supercapacitors, and these results are also...
Applicable to MSCs.\textsuperscript{13,14} However, when the device size is changed into microscale, electrode architecture design is of great significance for high-performance MSCs.\textsuperscript{1,15,16} A rational electrode design for MSCs should fulfill the following requirements: (i) high mass loading of electrochemical active materials to ensure high capacitance; (ii) better conductivity and lower charge transfer resistance for higher rate capability; (iii) enlarged surface area to provide abundant reaction sites; (iv) fast ion and electron transport pathway; (v) small enough device volume to be compatible with microelectronics.

As shown in Figure 2, recently emerged smart design strategies of electrodes can be summarized into three categories due to the different topologies of electrode structures. Their performances have been evaluated comprehensively in comparison with conventional MSCs. As depicted in Figure 2A, layer-by-layer (LbL) technique simply stacks many hybrid bilayers together in

![Electrode materials](image1)

![Current collector](image2)

(A) Conventional

![Areal capacitance](image3)

![Areal energy density](image4)

![Areal power density](image5)

![Cycle retention](image6)

(B) LbL

![Areal capacitance](image7)

![Areal energy density](image8)

![Areal power density](image9)

![Cycle retention](image10)

(C) Scaffold

![Areal capacitance](image11)

![Areal energy density](image12)

![Areal power density](image13)

![Cycle retention](image14)

(D) Rolling origami

![Areal capacitance](image15)

![Areal energy density](image16)

![Areal power density](image17)

![Cycle retention](image18)

**Figure 2** Schematic illustration of state-of-the-art smart design strategies of electrodes: (A) Conventional, (B) layer-by-layer (LbL)-assembled, (C) scaffold-assisted, (D) rolling origami-based, with their electronic/ionic diffusion capabilities and the corresponding electrochemical performance, respectively.
a regular order to enlarge the mass loading of electrode materials without increasing the cell resistance, thereby ensuring the balance between improved mass loading and sufficient conductivity.\textsuperscript{17,18} Eventually, an enhancement of electrochemical performance was obtained.\textsuperscript{19–21} Unfortunately, it still suffers from inferior volumetric energy density due to the compromise of device thickness for higher electrode material mass loading.\textsuperscript{22} As shown in Figure 2B, scaffold-assisted three-dimensional (3D) electrode design imposes the use of the third dimension to maximize the utilization ratio of footprint area. The usage of 3D technology offers enough space for high mass loading of electrode active materials and completely electrolyte infiltration without dead volume in the binder-free and self-support electrodes. Simultaneously, nanostructures enlarge the electrode/electrolyte interface and shorten the ion diffusion pathways with facilitated fast ionic transport kinetics. At the same time, the conductivity and mechanical robustness are improved due to the usage of a scaffold, resulting in comprehensive optimization of energy storage capabilities.\textsuperscript{23} As a matter of fact, scaffold-assisted 3D electrode design is a straightforward and effective method to possess both advantages via the combination of scaffold and 3D technology.\textsuperscript{14} In the end, a comprehensive enhancement of electrochemical properties has been achieved accompanying with good mechanical robustness to overcome the damage both in the integration process and practical applications.\textsuperscript{24–26} Unfortunately, for MSCs based on LbL or scaffold-assisted 3D electrode design, it is still not small enough to meet the application requirements of micro-intravascular implants for medical treatment. In this case, rolling origami (Figure 2C) is considered as a good alternative, which can dramatically scale down the device size and provide sufficient volumetric energy density and cycle retention.\textsuperscript{27,28} Moreover, durable enough mechanical properties for self-protecting in practical applications are maintained as miniaturized intravascular implants in the human body.\textsuperscript{29} Although the electrochemical performances of rolling origami-based MSCs are not outstanding when compared with MSCs based on LbL and scaffold-assisted electrode design, excellent volumetric energy density, and robustness capabilities are more needed for miniaturized intravascular implant applications.

It is worth mentioning that up to now there is no perfect strategy reported to meet the requirements of various aspects of electrochemical performance. Furthermore, it is important to be pointed out that these smart design strategies of electrodes are utilized flexibly for different application scenarios, and the combination of different design elements in one device is another particularly promising avenue to satisfy the performance requirements. Another point is that it is important to consider the areal normalization performance of MSCs, just like MBs, the metrics used to normalize the energy storage performance of supercapacitors are not suitable for MSCs within a limited footprint anymore. Owing to the utilization of low-volume active materials for charge storage, it is more significant to evaluate the power or energy performance of miniaturized supercapacitors based on footprint area or surface properties rather than gravimetric parameters.\textsuperscript{8,9} That means gravimetric values are meaningless for MSCs. Considering this, capacitance, energy, and power densities are reported in mF/cm\textsuperscript{2}, \(\mu\text{Wh/cm}^2\), and mW/cm\textsuperscript{2}, respectively, in this review.

### 3 | LBL-ASSEMBLED ELECTRODE DESIGN FOR MSCS

Increasing the mass loading of electrochemical active material per unit area of MSCs is of great feasibility to drive the inferior energy storage capability as described in the previous section. It is worth mentioning that pseudocapacitive materials generally suffer from generic conductivity. However, with the same device capacitance \((C)\), the time constant \((t)\) also exhibits properties proportional to the cell resistance \((R)\) in the same device \((t = RC_{\text{MSC}})\). Consequently, with the same surface capacitance, the higher mass loading, the higher cell resistance, the higher the time constant, and the lower the power performance. It can be concluded that minimizing the cell resistance plays a crucial role in achieving the trade-off between capacitance and power capabilities of MSCs with thick electrodes.

The LbL process is a prevalent cyclic process that alternately deposits functional thin films of multiple materials onto various substrates with nanometer precision.\textsuperscript{17} The LbL electrode offers many benefits: (i) providing hybrid thin films with a regular order, (ii) balancing the requirements between improved mass loading and insufficient conductivity of thick electrodes without dead volume (Figure 3)\textsuperscript{30–33} (iii) exhibiting good compatibility with most deposition techniques, and (iv) lowering the charge transfer resistance to enhance the rate capability.\textsuperscript{18} Additionally, electrodes based on the LbL design show much popularity in the field of electronic miniaturization due to enormous advantages of thin-film technology, including the ease of material synthesis/deposition, the well-developed fabrication (such as patterning and lithography), and integration technique in the semiconductor field. Up to date, a variety of methods for depositing LbL multilayered functional composite electrodes have been investigated to produce high-performance MSCs, which
are summarized in Table 1.\textsuperscript{19–22,34–43} In addition to electrode materials and deposition techniques, the electrochemical properties related to device energy/power density, cyclic stability, number of layers and electrode thickness are also shown. To further clarify and highlight the performance improvement contribution brought by this LbL electrode design, three representative reports are demonstrated in Figure 4.

The LbL is widely used in various fields for its ability to fix different layers together via electrostatic interaction, ionic charge transfer, covalent bonding, or hydrogen attachment.\textsuperscript{44} The LbL-based self-assembly method provides a platform for arranging different functional components with nanometer precision by introducing specific functional groups or surfactant molecules, following with better interface strength, enlarged accessible active area, and higher conductivity.\textsuperscript{45} For example, the Choi's group\textsuperscript{19} reported a typical LbL-assembled hybrid multilayer film, in which bulky high-energy ligand-stabilized manganese oxide (MnO) and indium tin oxide (ITO) nanoparticle (NP) arrays are fixed together by a ligand exchange reaction between native ligands (e.g., oleic acid [OA], oleylamine [OAm], and octanoic acid [OCA] ligands) and multidentate tricarballylic acid (TC). The resulted film did not contain organics or unnecessary electrochemically inactive components (Figure 4A).\textsuperscript{19} It is found that the molecular linker acts as a ligand to bond all adjacent NPs, which apparently minimizes the separation distance between pseudocapacitive NPs. Moreover, benefiting from the LbL assembly, the ITO NPs inserted between MnO layers significantly reduce the charge transfer resistance, thereby well alleviating the trade-off between areal capacitance and rate capability. Eventually, this flexible multilayer film (1.3 μm) exhibits a superior area-normalized capacitance of 41 mF/cm\textsuperscript{2} at 0.1 mA/cm\textsuperscript{2} and the corresponding areal power and energy densities of symmetric solid-state MSCs are 113 μW/cm\textsuperscript{2} and 0.82 μWh/cm\textsuperscript{2}, respectively.

There are also numerous conventional technologies that can meet the requirements of LbL composite electrodes for well-made thin films, including immersive, spin, spray, electromagnetic, fluidic, vacuum, and dewetting assembly (Table 1).\textsuperscript{31} Compared with these techniques, electrodeposition cooperated with the sputtering technique shows irreplaceable advantages in energy storage application. It addresses the challenge of utilizing versatile electrode materials, pseudocapacitive metal oxide materials (such as MnO\textsubscript{2} and RuO\textsubscript{2}), and conductive polymers (e.g., polyaniline and polypyrrole) for instance, to manufacture large-scale conformal films. Simultaneously, it can also provide fast, convenient, low-cost, and high-precision MSCs manufacturing. Accordingly, it is considered as one of the promising strategies to fulfill the demands of microelectronic energy storage systems. Case in point, a 3D interdigital stacked MSC with sputtered Au as the conductive layer and electrodeposited MnO\textsubscript{2} as the pseudocapacitive layer was demonstrated (Figure 4B).\textsuperscript{20} This vertical LbL configuration effectively increases the face-to-face contact area between each layer, thereby improving electron transport and electrolyte ion diffusion, thus enhancing the pseudocapacitive performance of MnO\textsubscript{2}. In addition, benefiting from simple optimization of deposition parameters, the hybrid LbL electrode in MSC possesses controllable areal capacitance and energy density. Consequently, directly rising the number of bilayers to three (1.6 µm) enlists the enhancement of the areal capacitance of MSCs based on the Au-MnO\textsubscript{2}-Au sandwich electrode from 4.3 to 11.9 mF/cm\textsuperscript{2} without increasing the total footprint area.

Moreover, unlike traditional LbL techniques (e.g., dipped solution adsorption), coupled with strong adhesion between the hybrid layers, the electrodeposition process is completed within several minutes, which has a huge industrial application potential. Unfortunately, it is important to note that if the desired materials (such as reduced graphene oxide) have a low charge density and cannot be layered, then electrodeposition is not applicable. In this case, employing these materials as ink to assemble MSCs via 3D printing technology is an implementable alternative.\textsuperscript{43–46} The 3D printing technique is recognized as one of the next-generation manufacturing techniques for its utilizing of 3D space to further improve the integration of MSCs, thereby achieving well-established voltage and capacitance within the footprint area of a device.\textsuperscript{47–49} More recently, Hu and coworkers\textsuperscript{21} reported 3D structured MSCs by combining inkjet printing and direct ink writing to print electrode
| Electrode materials | Deposition techniques | Device thickness (μm) | Layer number | Device capacitance (mF/cm²) | Peak energy density (μWh/cm²) | Peak power density (mW/cm²) | Device topology | Electrolyte/cell voltage | Cyclic stability | Ref. |
|---------------------|-----------------------|-----------------------|--------------|-----------------------------|-------------------------------|-------------------------------|----------------|--------------------------|----------------|-----|
| MnO/TC/ITO          | Ligand mediated       | 1.3                   | 50           | -                           | 0.82                          | 113 (μW/cm²)                 | Stacked        | PVA/LiCl/1.8 V            | 76% (5000)       | 19  |
| MWNT/Mn₃O₄         | Ligand mediated       | 0.22                  | 20           | 0.63                        | 2.4 (mWh/cm²)                 | 8 (W/cm²)                    | Interdigitated | PVA/H₂SO₄/0.8 V           | 90% (10,000)      | 34  |
| Ti₃C₂Tx MXene/rGO   | Ligand mediated       | ~3–5                  | -            | 391.2 (F/g)                 | 42.1                          | 61.1 (W/cm²)                 | Interdigitated | 3 mol/L H₂SO₄             | 98% (10,000)      | 35  |
| Ti₃C₂Tx MXene/TAEA  | Self-assembled        | ~0.085                | 40           | 4.8                         | 5.1 (Wh/L)                    | 4400 (W/L)                   | Stacked        | PVA/H₂SO₄/0.8 V           | 90.3% (10,000)    | 36  |
| Fe₃O₄/MCT/MnO/MCT   | Ligand mediated       | 0.35//0.34            | 60           | 179.2                       | 80.7                          | 3.4501 (mW/cm²)              | Fiber(asymmetric) | PVA/Na₂SO₄/1.8 V          | 92.3% (5000)      | 37  |
| AG/EG               | Vacuum filtration     | 20                    | 5            | 89.5                        | 0.52                          | 18.9 (W/cm²)                 | Interdigitated | PVA/H₂SO₄/0.8 V           | 99.6% (10,000)    | 22  |
| EG/PPY-Gr           | Vacuum filtration     | 5                     | 5            | 196                         | ~10.1 (mWh/cm²)              | ~1700 (mW/cm²)               | Interdigitated | PVA/H₂SO₄/0.8 V           | 66.7% (10,000)    | 38  |
| CuHCF/Gr//FeHCF/Gr  | Vacuum filtration     | 2                     | 20           | 19.84                       | 44.6                          | 16.88 (W/cm²)                | Interdigitated (asymmetric) | PVA/LiCl/1.8 V  | 96.8% (5000)               | 39  |
| Prussian-blue       | Immerser              | 0.09                  | 90 cycle     | 4.77                        | 12.1                          | -                            | Interdigitated | PVA/H₂SO₄/0.8 V           | 85% (10000)       | 40  |
| MnO₂/Au             | ED and sputtering     | 1.6                   | 7            | 11.9                        | -                             | -                            | Interdigitated | PVA/LiClO₄/0.8 V          | 67.9% (1000)      | 20  |
| PPY/MoO₃//Na₀.₅MnO₂  | ED                    | -                     | 20           | 398 (F/g)                   | 72.7 (Wh/kg)                 | 343 (W/kg)                   | Single electrode (asymmetric) | 5 mol/L LiCl/2.2 V | 92.3% (10,000)             | 41  |
| GMP/PEDOT:PSS       | Inkjet-print          | 10                    | 220          | 10                          | ~1                            | -                            | Interdigitated | PVA/H₂SO₄/0.8 V           | 80% (2000)        | 42  |
| CNT/PVA-H₃PO₄      | Inkjet print and direct ink writing | 273                  | 19           | 76                          | 6.38                          | 2.46                         | Stacked        | PVA/H₃PO₄/0.9 V            | 95% (10,000)      | 21  |
| rGO                 | 3D print              | 4.5                   | 4            | 38.4 (F/cm³)                | 7.6 (mWh/cm³)                | 30 (mW/cm³)                  | Interdigitated | PVA/H₂SO₄/0.8 V           | 53% (10,000)      | 43  |

Abbreviations: AG, nanoporous activated graphene; EG, electrochemically exfoliated graphene; G, graphene; GMP, graphene/MnO2/PANI; MCT, metallic cotton thread; MXene, 2D transition metal carbides and nitrides; PEDOT, PSS, poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate); PPY, polypyrrole; TAEA, tris(2-aminoethyl) amine; TC, multitendate small linker.
materials and electrolyte LbL without postprocessing (Figure 4C). The single stacked fully printed MSC is constructed by printing carboxyl-modified carbon nanotube (CNT) on the substrate as an electrode, then writing polyvinyl alcohol (PVA) electrolyte ink onto CNT film and following with another layer of CNT electrode. Due to their shear-thinning rheology behavior, PVA-based electrolytes can fulfill the excellent compatibility requirements for direct writing without the thermal process. For multiple MSC devices connected in parallel, when the number of bilayers is increased by directly repeating the above-mentioned LbL-based process, the footprint utilization ratio increases and the series resistance decreases, which is consistent with the previous reports. Finally, five bilayers based MSC lowers the series resistance from 10 Ω cm² (single stacked MSC) to 4 Ω cm² and reaches a remarkable areal capacitance of 76 mF/cm² at 1 mA/cm² which is five times...
higher than that of single one (14.7 mF/cm² at 0.2 mA/cm²) and exhibits 95% of the initial areal capacitance after 10,000 cycles.

The LbL deposits different functional thin films to construct a bilayer hybrid material, thereby resulting in a composite material by further repeating these steps. In this context, the resulted composite material possesses the emphasized properties of the bilayer hybrid material. Generally, the bilayer material can be composed by active/material, active material/solid-state electrolyte, and two different active materials. It is noteworthy that the construction and material properties of LbL-based electrode relies on the manufacturing techniques of thin film deposition to some extent (Table 1). Vacuum filtration is a general and effective method to transform nanoflacks into thin-film without obvious defects. Ligand mediated is considered as a promising self-assembly method to arrange different material as bilayer via the interface-specific functional groups or surfactant molecules, which accomplishes the LbL assembly in molecular level and following with vacuum filtration to obtain the target composite material. Ultimately, ligand-mediated endows the resultant thin film with better interface strength, enlarged accessible active area, and higher conductivity. However, unlike the thin film manufactured by electrochemical deposition or chemical vapor deposition techniques, the film obtained by vacuum filtration suffers from inferior physical and chemical properties due to the existence of numerous defects on the edge of each nanoflacks. In comparison, the 3D printing technique is a more versatile method to construct hybrid materials via changing the type of inks and depositing the materials onto complex substrates, as shown in Figure 4C. However, suitable inks of active materials are still limited and the printing resolution is also needed to be further improved.

Although significant progress have been achieved of MSCs based on LbL-based electrode design strategy, there are still some key aspects, to which need to be paid high attention: (i) considering the matching degree of the thermal properties of each component materials to avoid the separation of thin films during the manufacturing and charge-discharge processes; (ii) preventing the collapse of bilayer materials caused by volume expansion during the charging-discharging process, thereby resulting in compromise of electrode stability; and (iii) theoretical simulation and analysis to ensure optimized thickness parameters of each thin film to obtain maximum mass loading and good enough conductivity at the expense of minimum device thickness addition. Nevertheless, it has to be pointed out that the LbL-based assemble is not compatible well with the MSCs in stacked topology although the LbL technique is simple and effective to enhance the performance of MSCs. Since the out-layer materials act as a barrier layer in this context, the reaction efficiency of the interlayer with electrolyte will be low to some extent. The LbL-based electrode design is a highly compatible strategy ensuring a good combination with various techniques. With the continuous development of new materials and new technologies, LbL-based electrode design will be an indispensable part of the future smart design of electrodes for MSCs.

4 | SCAFFOLD-ASSISTED 3D ELECTRODE DESIGN FOR MSCS

From an energy storage mechanism point of view, there is now a growing realization that improving the surface area to volume ratio via 3D electrode design is a basic but effective strategy. Compared with 2D geometry, it is noted that 3D electrode design takes the advantage of longitude. When using the optimized parameters of the distance between two structures and the thickness of the structure, the space within a limited footprint area can be better utilized. In this context, a list of advantages has been achieved: (i) enlarging the electrode/electrolyte interface reaction area with high area enhancement factor (AEF) to obtain more active sites; (ii) facilitating fast ions and electrons transport kinetics; (iii) shortening diffusion pathways; (iv) ensuring no dead volume in the binder-free and self-support electrode; and (v) offering enough space for high mass loading and complete infiltration of electrolyte compared to the interdigitated planar topology. Nevertheless, 3D nanostructured active materials still suffer from some drawbacks, such as inferior robustness and direct adverse effects on the electrode/electrolyte interface during the charge–discharge process, which severely hinders the energy storage performance of 3D miniaturized energy storage devices.

In comparison to the in-situ grown 3D freestanding electrode materials mentioned above, fabricating nanostructured 3D scaffolds and following with the conformal deposition of electrode materials are attractive (Figure 5). Normally, metallic and carbonaceous materials can be fabricated into conductive scaffolds with good mechanical stability as current collectors for supercapacitors. These robust and conductive scaffold enlists to utilize pseudocapacitive materials, which have high theoretical specific capacitance but low electrical conductivity, as electroactive materials for MSCs. Simultaneously, from a structural point of view, since the
active materials are deposited in a conformal manner, the 3D nanoporous structure of the conductive current collector plays a key role in the fabrication process of heterogeneous hierarchical electrodes. Accordingly, the composite electrodes based on 3D scaffold obtain strengthened mechanical stability, better conductivity, sufficient ionic rapid transform pathway (Figure 6), and meanwhile possess the advantages of 3D electrodes as previously demonstrated. Compared with the planar geometry, 3D electrode exhibits a high AEF due to the synergy of 3D scaffold and conformal deposition. Unfortunately, the construction of scaffold inevitably leads to a compromise in volume and correspondingly lowers the mass loading of active materials to some extent. However, because of the high conductivity of the electrodes endowed by scaffold, materials with a high theoretical specific capacitance but insufficient conductivity can be deposited. And the limited volume for depositing active materials can be addressed in a simple way. For example, by increasing the length of nanotube-like nanostructures while keeping other parameters unchanged, it is possible to achieve an increased mass loading and a higher AEF at the same time. In this case, the 3D scaffold allows high rate electronic performance of the hierarchical electrodes without inducing kinetic limitations. To further clarify the impact of scaffold-assisted 3D electrode design in MSCs, recent reported MSCs are summarized in Table 2. In addition, three representative reports are illustrated in Figure 7 to highlight the contribution of this unique electrode design both in electronic performance and application in IoT network.

To significantly enhance the electronic performance of miniaturized energy storage devices, a particularly promising avenue is to predict the AEF of the 3D scaffold and fabricate it in a precise way, following with conformal deposition of electroactive materials on the surface. Due to the same technological mechanism and roadmap, more than 17 years of intensive investigation on 3D electrode construction of lithium-ion solid MBs allows the rapid upscaling of the 3D MSCs design in the last 10 years. Silicon has been spotlighted as a prevalent scaffold material, because of its outstanding robustness property and well-developed fabrication techniques (such as photolithography), based on which the influence of nanostructure geometry on energy storage performance has been intensively studied. The AEF has been proposed and defined as the ratio between the surface area of a 3D electrode ($S_{3D}$) and the footprint area on a planar substrate ($S_{planar}$).

**FIGURE 5** Schematic representation of micro-supercapacitor consists of 3D scaffold and conformal active material film in planar topology and the cross-section of the electrode highlights the nanostructures of the scaffold-assisted electrode unit.

**FIGURE 6** Schematic comparison of ion diffusion pathways between (A) conventional thick film electrode and (B) emerging scaffold-assisted electrode with conformal thin-film active materials.
### Electrochemical performance of MSCs based on 3D scaffold-assisted electrode design

| Electrode materials | Active materials | 3D scaffold | Material thickness (μm) | Main techniques | Electrode capacitance (mF/cm²) | Peak energy (μWh/cm²) | Peak power (mW/cm²) | Device topology | Electrolyte/cell voltage | Cyclic stability | Ref. |
|---------------------|------------------|-------------|-------------------------|-----------------|--------------------------------|----------------------|-------------------|----------------|--------------------------|----------------|------|
| MnO₂                | Si micropillars  | 0.275       | PL, ALD, ED             | 670             | -                              | -                    | -                | Single electrode | 0.5 mol/L Na₂SO₄/0.8 V | 85%            | (15,000) |
| MnO₂                | 3 in. Si microtube | 0.5        | PL, ICP/RIE, ALD, ED   | -               | 10                             | 20                   | 0.7               | Interdigitated   | 0.5 mol/L Na₂SO₄/0.8 V | 80%            | (15,000) |
| RuO₂                | Si microtube     | 0.427       | DRIE, ALD, ED          | 4500            | -                              | -                    | -                | Single electrode | 0.5 mol/L H₂SO₄/1 V | 90%            | (10,000) |
| GNW/RuO₂            | Si               | 0.78        | DRIE, MPECVD           | -               | 15.1                           | 2.49                 | 0.7               | Spiral          | PVA H₃PO₄/1 V | 90.2%          | (3000) |
| MnOₓ                | PSiNWs           | -           | CVD, MACE, ED         | 635 (F/g)       | 37 (mWh/cm³)                   | 4 (W/cm³)            | 0.7               | Interdigitated   | 2 mol/L EMIM- TFSI/3.6 V | 82%           | (10,000) |
| δ-MnO₂              | AuNPs            | 0.75        | Chemical dealloyed, ED | 922 (F/cm³)    | 24.3 (mWh/cm³)                 | 295 (W/cm³)          | 0.7               | Interdigitated   | 1 mol/L Na₂SO₄/0.8 V | 88%           | (20,000) |
| MnO₂                | ITONWs           | -           | CVD, ED               | -               | 26.94                          | 15.07                | 0.7               | Interdigitated   | 1 mol/L Na₂SO₄/0.8 V | 61.1%          | (20,000) |
| PPY//MnO₂           | SnO₂NT           | -           | AAO, ALD, ED          | 260 (F/g)/910(F/g) | 27.2 (Wh/kg)                   | 24.8 (kW/kg)         | 0.7               | Interdigitated   | 1 mol/L Na₂SO₄/1.7 V | 80%           | (2000)   |
| MnO₂                | Ni nanorod       | 3           | AAO, ED               | 352             | -                              | -                    | -                | Single electrode | 1 mol/L Na₂SO₄/0.8 V | ~90%          | (5000)   |
| RuO₂·xH₂O          | Porous Au        | -           | HBDT, ED              | 3250            | 126                            | 7.9                  | -                | Stacked         | PVA H₃PO₄· H₄SiW₁₂O₄₀/ 0.9 V | 95%           | (2000)   |
| RuO₂ₙSₙ            | Porous Au        | ~100        | HBDT, ED              | 14,300          | 432 (mJ/cm³)                   | 421                  | 0.7               | Interdigitated   | PVA H₃PO₄· H₄SiW₁₂O₄₀/ 0.9 V | 100%          | (5000)   |
| MnO₂                | Wood carbon      | 10~15       | Carbonization, ED     | 4155            | 1600                           | 24 (W/cm²)           | 0.7               | Stacked         | PVA LiCl/1.8 V | 93%            | (10,000) |
| MnO₂                | Ni nanopore arrays | 0.1       | AAO, ED               | 570(F/g)        | -                              | -                    | -                | Single electrode | 1 mol/L Na₂SO₄/0.8 V | 83%           | (3000)   |
| Active materials | 3D scaffold | Material thickness (μm) | Main techniques | Electrode capacitance (mF/cm²) | Peak energy (μWh/cm²) | Peak power (mW/cm²) | Device topology | Electrolyte/cell voltage | Cyclic stability | Ref. |
|-----------------|-------------|-------------------------|----------------|-----------------------------|----------------------|---------------------|----------------|------------------------|----------------|-----|
| MnO₂            | FTO/AAO     | -                       | AAO, USP, ED   | 87.4                        | 1.56                 | -                   | Stacked         | 1 mol/L Na₂SO₄/0.8 V | 81.6% (3000)    | 70  |
| MnO₂            | FTO/AAO     | -                       | AAO, USP, ED   | 540                         | 2.36                 | 4.45                | Stacked         | 1 mol/L Na₂SO₄/0.8 V | 85.5% (5000)    | 71  |
| PPY/MnO₂       | SnO₂/AAO    | -                       | AAO, ALD, ED   | -                           | 160                  | 40                  | Stacked         | EMIM-TFSI/3 V      | 82.5% (10,000)  | 25  |
| PPY/MoO₃//Na₀.₅MnO₂ | Exfoliated graphite | -                  | Electrochemical exfoliation, ED, LbL | 398 (F/g) | 72.7 (Wh/kg) | 343 (W/kg) | Single electrode (asymmetric) | 5 mol/L LiCl/2.2 V | 92.3% (10,000) | 41  |
| Ni(OH)₂        | CuSe        | -                       | ED             | -                           | 5.4                  | 83.2                | Interdigitated   | PVA LiCl/1 V       | 100% (10,000)   | 71  |
| Hydrous-RuO₂   | CNW         | 6.4                     | PECVD, ED      | 1094                        | 49                   | 31.3                | Stacked         | PVA H₃PO₄//H₂SiW₁₂O₄₀/0.9 V | ~90% (2000)      | 72  |
| Ni(OH)₂        | GNW         | -                       | MPECVD, EB, electrochemical oxidation | 33.6 | 2.1 (mWh/cm³) | 5.91 (W/cm³) | Interdigitated | PVA H₂SO₄/1.3 V | 95.6% (10,000) | 73  |
| MnCO₃          | rGO framework | -                     | Immerse, LbL, hydrothermal | 320 (F/g) | -            | -                   | Stacked         | PVA LiCl/1 V       | 77% (5000)       | 74  |
| MnO₂            | LSG         | -                       | Laser scribing, ED | -                           | 42 (Wh/L)            | -                   | Stacked         | 1 mol/L Na₂SO₄/2.0 V | 96% (10,000)    | 75  |
| PPY            | GF          | -                       | Laser induction | 2412.2                      | 134.4                | 6.5                 | Interdigitated   | PVA H₂SO₄/1.3 V | 95.6% (10,000) | 76  |
| Fe₂O₃//CoMoO₄   | GF-CNT      | -                       | CVD, ALD       | 370.2 (Fe₂O₃)               | -74.7 (Wh/kg)        | -11.2 (kW/kg)      | Stacked         | 2 mol/L KOH/1.2 V | 95.4% (50,000)   | 77  |
| GMP            | Au pillars  | 10                      | Inkjet print, LbL | 10                          | -1                   | -                   | Interdigitated   | PVA H₂SO₄/0.8 V | 80% (2000)       | 42  |
| MnO₈-PEDOT:PSS  | Stainless steel | -                   | 3D print, Co-ED | 1520                        | -                    | -                   | Single electrode | 0.25 mol/L LiTFSI/1 V | 80% (1600)      | 78  |

(Continues)
### Table 2 (Continued)

| Electrode materials | Material thickness (μm) | Main techniques | Electrode capacitance (mF/cm²) | Peak energy (μWh/cm²) | Peak power (mW/cm²) | Device topology | Electrolyte/cell voltage | Cyclic stability | Ref. |
|---------------------|-------------------------|-----------------|-------------------------------|----------------------|---------------------|------------------|--------------------------|------------------|------|
| MnO₂                | Graphene aerogel         | 3D print, ED    | 44,130                        | 1560                 | -                   | Stacked          | 3 mol/L LiCl/2.2 V       | 92.9% (20,000)  | 47   |
| PPY                 | Graphene aerogel         | 3D print, freeze-drying, annealing | 2000                       | 110                  | -                   | Stacked          | 2 mol/L KOH/0.8 V       | 75% (5000)      | 79   |
| Graphene/MWCNT      | -                       | 3D print, freeze-drying | -                           | 53                   | 1.54                | Stacked          | 6 mol/L KOH/0.8 V       | 90% (10,000)    | 80   |
| PPY                 | Ti₆Al₄V                  | SLM, ED         | -                             | 213.5 (Wh/m³)        | 15 (kW/m³)          | Stacked          | PVA H₃PO₄/1 V           | 78% (1000)      | 81   |
| Mxene-AgNW-MnONW-C₆₀| -                       | 3D print, LbL, unidirectional freezing, freeze-drying | -                           | 19.2                 | 58.3                | Interdigitated   | PVA KOH                 | -                | 26   |

Abbreviations: ALD, atomic layer deposition; CNW, carbon nanowall; CVD, chemical vapor deposition; DRIE, deep reactive ion etching; EB, electron beam; ED, electrodeposition; EMIM-TFSI, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; FTO, fluorine-doped tin oxide; GF, graphene framework; GMP, graphene/MnO₂/PANI; GNW, graphene nanowalls; HBDT, dynamic hydrogen bubble template; LSG, laser-scribed graphene; MACE, metal-assisted chemical etching; PL, photolithography; PPY, polypyrrole; SLM, selective laser melting; USP, ultrasonic spray pyrolysis.
For example, the AEF of 3D architecture in tubular topology is given by:

\[ \text{AEF} = 1 + \frac{(P_{\text{out}} \times d_{\text{out}}) + (P_{\text{in}} \times d_{\text{in}})}{\text{SP}^2}, \]

where SP is the structure pitch which means the sum of the outer diameter \( D_{\text{out}} \) of a single tube and the interspace between two tubes, \( D_{\text{in}} \) refers to the inner diameter, \( P_{\text{in}} \) and \( P_{\text{out}} \) present the inner and outer perimeter, respectively (Figure 7A). Likewise, \( d_{\text{in}} \) and \( d_{\text{out}} \) are the inner and outer depth, respectively.

Meanwhile, the relationship between capacitance \( C \) and surface-active area \( S \) of device can be illustrated clearly according to:

\[ \text{AEF} = \frac{C_{3D}}{C_{\text{planar}}} = \frac{S_{3D}}{S_{\text{planar}}}. \]

More recently, Asbani and coworkers\(^{24}\) demonstrated an approach to enhance the capacitive performance of
3D MSCs via enlarging the depth of the tube through deep reactive ion etching (DRIE) to optimize the AEF and improve the amount of active materials through increasing the CV cycles of the electrodeposition process. Eventually, an ultrahigh capacitive performance electrode based on 170 µm-depth silicon microtubular scaffold (AEF = 66) coating with 427-nm-thick RuO₂ film was obtained (Figure 7A). The fine-tuned 3D electrode exhibits a remarkable capacitance of 4300 mF/cm² at 100 mV/s and delivers ~90% of initial capacitance after 10,000 cycles.

The template-assisted method is recognized as another full-fledged approach to achieve 3D micro/nano-structured architectures such as nanowires,⁸⁵ nanotubes,⁵⁵ nanopillars,⁴²,⁶⁰ nanorods,⁶⁶ nanosheets/nanowalls, and so forth. Moreover, the highly ordered nanostructures based on template-assisted methods offer a platform for a better understanding of microfluid mechanics and thermodynamic dynamics in MSCs and MBs.⁸⁶ Normally, the template-assisted nanostructure manufacturing process involves two steps: (i) depositing conformal electroactive materials onto the surface of the template and (ii) removing the template via chemical reaction or other processes (depending on the materials of templates) to obtain the desired nanostructures. Case in point, anodic aluminum oxide (AAO) template method is well known for its versatile and simple fabrication process, which possesses significant potential for 3D nano- or microstructured architectures for miniaturized energy storage applications.⁸⁷ Due to a low surface area of contact, the desired active materials cannot be layered onto the surface of nanowire-based scaffold. Thus, to realize both high energy density and high capacity via enlarging AEF, nanopillar (Figure 8A) and nanotube (Figure 8B) are better alternatives. Unfortunately, nanopillar/nanotube structures still suffer from inherent drawbacks: (i) nanopillar occupies too much volumetric space, leading to a low areal loading of active materials, and (ii) nanotube/nanowire with high aspect ratio suffers from insufficient robustness or mechanical stability with limited cycle life time. Notably, when the length of nanopillar/nanotube is increased to achieve high aspect ratio for improving the mass loading of active materials, their arrays will suffer from agglomeration. In contrast, the agglomeration existing in nanostructure arrays will inevitably deteriorate the device performances such as ion transport and cyclability. In this case, the configuration of metal nanopore arrays as a conductive scaffold through the two-step replication AAO method has attracted much attention as an efficient strategy, enabling to address the mentioned drawbacks of high-performance MSCs (Figure 8C).²³ Likewise, it is worth mentioning that Lei's group²⁵ reported a high-energy MSCs recently, which addressed the nanostructure collapse issue smartly by utilizing ultrathin honeycomb alumina in nanopore array geometry with only 16 ± 2 nm cell-wall-thickness as stiff nanoscaffold (Figure 7B). These aligned pores in honeycomb alumina nanoscaffold (HAN) facilitate the ion-diffusion and liquid electrolyte infiltration, and improve the performance of both energy and power from a structural point of view. Figure 9 shows the typical MSCs based on scaffolds with nanopillar array (A) and nanopore array (B). Both of them offer sufficient
mechanical properties for devices, especially in assembly process. As for evaluating the utilization ratio of footprint area, the AEF of a nanopore array is equal to that of a nanopillar array with the same structural parameters. Thus, the AEF of a nanopore array (such as hexagonal and square cell) is given by:25

$$AEF = \frac{6 \times d \times h}{s^2 \times \sin \theta},$$

(3)

where $d$ and $h$ represent the cell diameter and depth, respectively; $s$ is the distance between the centers of two cells; and $\theta$ is the angle of the patterns on AAO templates. For instance, the $\theta$ of a hexagonal cell is 60°.

These exciting features of the ultrathin honeycomb alumina nanoscaffold (depth is 25 µm) ensure a good balance between robustness and enhanced active area (AEF = 240), allowing the volume to be enlarged to obtain optimal amount of electrochemically active materials and sufficient reaction between active materials and electrolyte to maximize the overall performance of MSCs. A 12-nm-thick tin oxide (SnO$_2$) conformal film was coated onto the intercell of the alumina nanoscaffold through atomic layer deposition (ALD) to overcome the inherent insulating nature of AAO template.83 Regardless of intricacy and aspect ratio, this technique enlists depositing thin and pinhole-free layers on complex substrates. This is widely investigated as a prevalent technique to fulfill the structural and chemical requirements for advanced MBs and MSCs application.24,45,60,61,84

Consequently, benefiting for the synergy of ALD and electrodeposition technique, the PPy//MnO$_2$ asymmetric MSC based on SnO$_2$/AAO scaffold (AEF = 240) accomplishes effective ion migration and ample electroactive surface area within a limited footprint area, finally delivering a high device capacitance of 128 mF/cm$^2$ at 0.5 mA/cm$^2$. Simultaneously, the peak energy and power densities are 160 µW/cm$^2$ and 40 mW/cm$^2$, respectively, coupling with a considerable cycling life span (82.5% of initial capacitance after 10,000 cycles).

The 3D printing technique is a promising bottom-up manufacturing technology that is capable for constructing versatile 3D geometrically complex configurations. The 3D printing technique exhibits significance for scaffold-assisted 3D electrode design of composite electrode construction over the past decade.88–91 Deposition and conversion are two typical construction strategies of refined scaffold-based electrodes via the 3D printing technique.24,45,60,61,84 Deposition means that the scaffold is constructed firstly, and then a conformal active material layer is deposited on the surface. Nevertheless, conversion strategy is more intriguing, in which the active materials are completed by additional posttreatments such as annealing and freeze-drying after printing, and thus to meet maximum functionality. More recently, Li and the coworkers26 reported a 3D-printed MSCs constructed by the pseudoplastic nanocomposite fine gel (Ti$_3$C$_2$Tx Mxene nanosheets, manganese dioxide nanowire, silver nanowires, and fullerene, Mxene-AgNW-MnONW-C$_{60}$ gel). As shown in Figure 7C, after complex preparation steps of the printable nanocomposite ink, the fine gel is deposited onto the substrate, and finally the honeycomb porous scaffold is obtained through the dual functions of unidirectional freezing as well as freeze-drying processes. Eventually, the MSC is accomplished when the gel electrolyte is dropped into the projection region of the versatile electrode, thus delivering an areal capacitance of 216.2 mF/cm$^2$ (at 10 mV/s) higher than reported stretchable MSCs and outstanding rate capability.85,93–95 And the areal energy density and power density are performed as 19.2 µWh/cm$^2$ and 58.3 mW/cm$^2$, respectively.

Although recent progress enable scaffold-assisted 3D electrode design to attract much attention, it is worth mentioning that scaffold-based research is still in its infancy and this versatile technique is not faultless. For scaffold-assisted MSCs, the main challenge is how to guarantee simultaneous enhancement of energy and power densities via careful optimization of scaffold
parameters. For instance, the enlarged diameter of nanopore array unit ensures enough space for more electrochemically active material mass loading and sufficient empty voids.\textsuperscript{52} The improvement of electrode material deposition results in enhancement of energy capability. Simultaneously, the empty voids ensure various advantages: (i) fully electrolyte infiltration for sufficient reactions between electrode materials and electrolyte; (ii) facilitating ion transport for high power capability; and (iii) avoiding the collapse of nanostructured electrode materials caused by volume changes during charge-discharge operation process. However, cell-wall-thickness is another parameter that should be considered to ensure the good enough conductivity and mechanical robustness of MSCs. In this case, to achieve a comprehensive enhancement of electrochemical properties and good mechanical robustness, for nanopore array-based MSCs, the parameters for diameter, the thickness of electrode material layer, and the cell-wall-thickness are imperative to be optimized carefully. In comparison, for MSCs based on nanopillar/nanotube 3D scaffold, the aspect ratio should be considered carefully. Enlarging the length of nanopillar/nanotube 3D scaffold is an alternative strategy to improve the mass loading, however, which comes at the expense of a much higher thickness of the device and a longer electron/ion diffusion distance. Worse still, too high aspect ratio is a negative factor for nanopillar/nanotube structures because long individual arrays would suffer from agglomeration, thereby resulting in the inevitable deterioration of device performances such as ion transport and cyclability. In this context, rational design of diameter and thickness parameters offers a promising pathway to address this problem.\textsuperscript{96,97}

For high-performance MSCs based on 3D scaffold-assisted design concept, the following aspects also should be considered: (i) advanced theoretical simulation and analysis are needed to further understand the precise correlation between electrochemical properties of MSCs and nanostructure parameters; (ii) higher conductive active materials are required to further minimize the volume of current collectors; and (iii) the capability of electrolyte to infiltrate into 3D scaffold-assisted electrode should be considered, especially for the solid-state electrolyte.\textsuperscript{98,99}

5 | ROLLING ORIGAMI-BASED ELECTRODE DESIGN FOR MSCS

Benefiting for a plethora of advantages to meet the ever-increasing requirements both for higher energy density and power density, 3D electrode design is regarded as one of the mainstream approaches from an architecture science and engineering point of view. Evolving in leaps and bounds of theoretical mechanics, geometry, origami mathematics and biomimetics in recent years, origami, the talented paper art, has garnered intense scientific interest for inspiring the in-situ transformation of planar functional films into 3D architecture.\textsuperscript{100,101} As one of 3D assembly methods, rolling origami has often been treated as an alternative to 3D manufacturing technology to effectively realize higher utilization ratio of the planar functional composite films, which can be exploited in numerous application fields, involving energy storage systems, sensors, robots, drug delivery, and so forth.\textsuperscript{102–105} Recently, rolling origami has been successfully applied into MSCs and MBs for achieving higher energy storage ability within a limited footprint area. MSCs based on rolling origami exhibit promising potential for next-generation high-performance miniaturized network applications. From 2000 onward, rolling origami (Figure 10) has been used to transform thin

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{rolling_origami.png}
\caption{Schematic comparison of ion diffusion pathways between conventional thick film electrode (A) and rolled-up electrode with conformal thin film active materials (B)}
\end{figure}
delaminated planar layers into 3D nanostructure geometry, and this controllable self-assembly process is supported by a reliable and model of elastic mechanics while the curvature of rolled-up nanomembranes can be calculated.\textsuperscript{106–109} The realization of this novel approach relies on the built-in strain relaxation by selective etching of the sacrifice layer, and thus the strained nanomembranes spontaneously assemble themselves into cylinder structures as 3D free-standing forms to stabilize their elastic energy. Since then, a variety of materials have been developed to compose a diversified material system as a precursor film to contain the properties for transform into cylinder geometry by this automated pick-and-place process.\textsuperscript{110} Generally, the precursor nanomembranes contain of the bottom substrate, sacrificial layer in the middle and functional layer on the top. The sacrificial layer implements the rolling origami, and the functional layer determines the applications. The major mechanical problem that would arise during the rolling process of MSCs is misassembly, which would result in wrong geometries due to the degrees of freedom, especially for nanomembranes with a high aspect ratio.\textsuperscript{111} Up date, there are two pathways to solve this mechanical problem. One is designing the proper pattern parameters of nanomembrane which would influence the rolling behavior in a symmetric releasing system, including the width, length, thickness, and rolling diameter.\textsuperscript{112,113} Another one is restraining the degrees of freedom via applying an external magnetic field.\textsuperscript{114} It directly increases the accuracy and achieves an assembly yield of more than 90%, especially for nanomembranes with a high aspect ratio to well match the target microstructure. Unique features endow rolling origami technique with better functionality and performance, for instance, (i) dramatically scaling down the device size with unique 3D geometry, (ii) offering sufficient ion diffusion pathways (Figure 10), (iii) exhibiting excellent applicability with electrode/electrolyte materials and fabrication techniques of planar MSC, and (iv) providing excellent fixation and mechanical properties to well accomplish the integration with microelectronic circuits. Moreover, advanced thin film deposition and full-fledged pattern techniques such as ALD, electron-beam physical vapor deposition (eB-PVD) and photolithography ensure the construction of rolled-up MSCs based on diverse material systems. Thus, a variety of advanced MSCs based on rolling origami are summarized in Table 3 and representative reports of rolled-up MSCs are illustrated in Figure 11.\textsuperscript{27–29,114–117}

Typically, as presented in Figure 11A, Wang and coworkers\textsuperscript{27} demonstrated a tubular MSC, in which poly (3,4-ethylenedioxythiophene) (PEDOT) is used as active electrode material and a bilayer based on swelling hydrogel layer and polyimide (PI) layer serves as versatile polymeric layer. After selectively chemical etching in potassium diethylenetriaminepentaacetic acid, the sacrificial layer is removed away, followed with the planar device detached from the substrate and transformed into tubular geometry via self-rolling assembly process due to the strain mismatch of the swelling hydrogel and PI. Accordingly, the obtained rolled-up tubular geometry allows efficient ion transport of PEDOT electrode in a greatly reduced footprint area, resulting in higher performance compared with previously reported electrolytic capacitors.\textsuperscript{115,117} with an areal capacitance of 82.5 mF/cm$^2$ at 0.3 mA/cm$^2$, the energy and power densities of 7.73 µWh/cm$^2$ (0.3 mA/cm$^2$) and 17.8 mW/cm$^2$ (45 mA/cm$^2$), respectively, as well as 94.1% capacitance retention after 5000 cycles. Furthermore, the polymeric framework in rolling origami is inherently robust, thereby leading to an efficient self-protection function against external high-pressure compression even up to 30 MPa. Unfortunately, it also demonstrated that tubular MSCs with lower PEDOT load have better self-protection capabilities, implying that a trade-off should be taken into account between energy and mechanical properties.\textsuperscript{118} It has nevertheless to be pointed out that the MSC-30 can still deliver high capacitance retention of 71.9% after suffering from 31.8 MPa compression 66 times, which proves that the MSCs based on rolling origami has excellent fixation and mechanical properties. Additionally, with the same fabrication process, Li and coworkers\textsuperscript{28} further utilized this PEDOT as a scaffold to electrodeposit MnO$_2$ and Fe$_3$O$_4$ to construct asymmetric electrodes for MSC (Figure 11B). Eventually, the energy density was enhanced to 28.69 µWh/cm$^2$ with a 91.8% capacitance retention over 12,000 cycles.

Benefiting from the ultrasmall volume and powerful self-protection mechanical properties, MSCs based on rolling origami not only exhibit versatile performances in microelectronic systems but also promote the development of biosupercapacitors (BSCs) for the personalized healthcare sector, such as tiny biocompatible intravascular implants and microrobots operating in the human body. Of note, most of MSC materials are undesirable to directly employed as BSCs in the human body because their toxic or corrosive. In comparison, materials used in BSCs are fully biocompatible and the existed bioelectrocatalysis in blood enables to compensate the self-discharge behavior. Thus, BSCs directly utilize blood as an electrolyte to accomplish the device operation as energy source in implantable autonomously working systems. Case in point, more recently, a rolling origami-based nano-biosupercapacitor (nBSC) was reported by Lee et al.,\textsuperscript{29} which contains 100-nm-thick poly (3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate)
| Materials | Mechanism | Main techniques | Device capacitance (mF/cm²) | Peak energy (μWh/cm²) | Peak power (mW/cm²) | Electrolyte/cell voltage | Cyclic stability | Ref. |
|-----------|-----------|----------------|----------------------------|-----------------------|---------------------|--------------------------|-----------------|------|
| Ti/Al₂O₃/Cr/Al₂O₃ | Strain relaxation | ALD | 0.2 | ~0.55 (Wh/kg) | 2000 (W/kg) | - | - | 115 |
| Au/RuO₂ | Strain relaxation | Deposition, chemical etching | 2.2 | - | - | 0.5 mol/L H₂SO₄/0.8 V | ~100% (1200) | 116 |
| HfO₂/TiO₂/Al₂O₃ | Strain relaxation | ALD, photolithography | 1.5 | - | - | - | - | 117 |
| PEDOT | Strain relaxation | Lithography, electrodeposition, chemical etching | 82.5 | 7.73 | 17.8 | 5 mol/L PVA LiCl/0.8 V | 94.1% (5000) | 27 |
| PEDOT-MnO₂//PEDOT-Fe₃O₄ | Strain relaxation | Spin-coating, lithography, electrodeposition | 88.6 | 28.69 | 39.47 | 5 mol/L PVA LiCl/1.5 V | 91.8% (12,000) | 28 |
| Al₂O₃/Ni/Cr/Al₂O₃/Ni/Cr(axial) | Magnetic field-assisted strain relaxation | Spin-coating, ALD, eB-PVD, RIE | 0.15 (axial) | - | - | 0.01 mol/L H₂SO₄ | - | 114 |
| Al/Al₂O₃/Al(radial) | | | 2.83 (radial) | - | - | - | - | |
| Cr/Au/PEDOT:PSS/PVA/PEDOT:PSS/Cr/Au | Strain relaxation | Spin-coating, ALD, eB-PVD, photolithography | ~0.6 (mF/mm³) | ~90 (nWh/mm³) | ~32 (μW/mm³) | Blood/1 V | ~70% (5000) | 29 |

Abbreviations: BMIMBF₄, 1-butyl-3-methylimidazolium tetrafluoroborate; eB-PVD, electron-beam physical vapor deposition; nBSC, nano-biosupercapacitor; PEDOT, poly(3,4-ethylenedioxythiophene); PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate); RIE, reactive-ion etching.
A bilayer of swelling hydrogel and PI applied at the bottom is a key element to result in 3D tubular geometry with a volume of only 1 nL due to the strain mismatch between them separating the entire device from the substrate after the selective etching process. Meanwhile, PVA is another key factor to ensure bioelectrocatalytic reactions in blood to tackle the rapid self‐discharge as a proton exchange separator. Because this PVA proton exchange separator enables to suppress the side redox reactions and to prevent self‐discharge via acting as an active barrier to inhibit the migration of protons from the bioanode to the biocathode. Moreover, bioelectrochemical reactions produced by enzymes and living cells in blood offer nBSCs an enhanced performance (Figure 11C). In the end, the tubular nBSC based on rolling origami delivers a specific capacitance of ~0.6 mF/mm³ at 20 nA while the corresponding energy and power densities are ~90 and ~32 μW/mm³ at 50 nA,
requirements of MSCs, the following aspects should attract considerable attention: (i) the carefully selected sacrificial layer material is needed to ensure the transform accomplishment from planar into 3D architecture; (ii) advanced theoretical simulation and analysis based on modeling are expected to illustrate the influences of rolling parameters on electrochemical, magnetic, and mechanical properties of rolling origami-based MSCs such as winding number and electrode material layer thickness; (iii) advanced active materials and the corresponding fabrication techniques are still limited; (iv) advanced electrolytes, especially for solid-state electrolytes and appropriate encapsulation, are required to ensure the device compactness; and (v) an enlarged number of windings of high aspect ratio nanomembranes is utilized to pursue more active materials. Directly increasing the thickness of the active material layer is an intuitive strategy for more mass loading. However, it has been demonstrated that tubular MSCs with lower mass loading have better self-protection properties. Nevertheless, excellent fixation and mechanical properties are also important for MSCs based on rolling origami in rational applications. For example, nBSCs implanted in the human body should possess robust enough mechanical capability to realize self-protection with a stable performance in blood flow. Thus, a trade-off between electrochemical and mechanical performances is necessary for MSCs based on rolling origami design concept. In addition, the electrolyte in these tubular MSCs is normally infiltration into the device when the assembly process is completed, however, there still exists dead volume to some extent due to the compact geometry. In the future, if conformal solid-state electrolyte can be deposited at electrode surface as discussed above, it can be a part of bilayers and realize the self-rolling together with other films.

6 | SUMMARY AND OUTLOOK

This review comprehensively summarizes the smart design strategies of electrodes toward enhancing the energy performance from a structural point of view based on reported MSCs over the past years. To meet the requirement of practical microelectronics, the footprint area of MSCs has been dramatically scaling down to several square millimeters. In this context, the smart design of electrodes is obviously more significant to sufficiently utilize the limited active material, for which the mass loading of MSC active material is even only one milligram. Given the present progress discussed in this review, the smart design of electrodes is a promising strategy to maximize the energy density
higher than those of many commercial MSCs without sacrificing power density and lifespan. Along with a limited footprint area, smart design strategies of electrodes ensure unique electrode structure topologies and sufficient utilization of active materials to meet the requirements for high-performance MSCs. However, so far, there is no perfect design strategy that enables electrodes to meet the requirements of various aspects of electrochemical performance for ideal MSCs. As an instance, LbL-based electrodes obtain an enhancement of electrochemical performance, but this comes at the expense of device thickness and results in an inevitably compromised volumetric energy density. For scaffold-assisted MSCs, a comprehensive enhancement of electrochemical properties and good mechanical robustness are achieved, but it comes at the expense of a much higher device thickness and a longer electron/ion diffusion distance, thereby resulting in unsatisfied device volume and a sacrificed fast charge capability. MSCs based on rolling origami show excellent volumetric energy density and robustness capabilities, while the areal electrochemical performance is insufficient. Of note, every smart design concept is utilized flexibly for different application scenarios. As mentioned, for miniaturized intravascular implant applications, excellent volumetric energy density and robustness capabilities are more needed. Simultaneously, the combination of LbL, scaffold-assisted and rolling origami in one device might be another particularly promising avenue to design electrodes to satisfy the performance requirements of advanced MSCs. Case in point, LbL and scaffold have been successfully combined together to achieve higher performance of MSCs.

As for the smart design of electrodes, it is important to keep in mind that high power and energy densities have always been the scientific pursuits for MSCs as alternatives for MBs. Unfortunately, despite a surge of new inspiring design concepts to enhance the performance of MSCs, they still suffer from low energy density. Developing MSCs based on the smart design of electrodes is very desirable and practically necessary to fulfill the fast-increasing requirements both on performance and device size. In fact, up to now, complete filling of solid-state electrolytes into MSCs still remains challenging and empty voids are still needed for better electrolyte infiltration. However, this comes at the expense of a lower mass loading which results in insufficient energy storage performance to some extent. Thus, it is obvious that the smart design principle of electrodes for MSC electrodes is to design and construct active materials, current collectors, and empty voids with optimized volume ratio, respectively, to make full use of the limited space, as depicted in Figure 12. In addition, there remain various infective factors that should be considered to successfully accomplish the transitioning of these MSCs from lab to markets such as manufacturing technology, electrolyte infiltration, advanced characterized techniques, advanced theoretical simulation, and analysis. These would be discussed in the following:

(i) Manufacturing technology. MSCs put forward much higher requirements on the nanoscale electrode manufacturing techniques on both accurately controlling structural geometries and active material properties. In this context, the 3D printing technique is a promising candidate which endows the predesigned electrode with various structures and morphologies via precise control of the fabrication parameters. However, suitable inks of active materials are still limited and the printing resolution is also needed to be further improved. Furthermore, to maintain the complex morphologies of current collectors/scaffolds, conformal deposition techniques of thin film are desired. The ALD technique is a suitable alternative to achieve this goal, which ensures controlling the thickness of active material layer at the atomic level. But the diversity of suitable active materials and the corresponding process technique are limited. In addition, further developed ALD processes the potential to accomplish the conformal deposition of solid-state and ceramic electrolyte in the near future. Thus, considerable research attention and efforts should be devoted into the issues of nanostructure construction and active material conformal deposition. Other than 3D print and ALD, lots of advanced constructing techniques of microelectronic devices are needed because a complete device manufacturing process requires a series of complex manufacturing steps. Thus, cost-effective manufacturing technologies are
desirable and practically necessary to realize the successful transitioning of MSCs based on the smart design of electrodes from the lab to the commercial market in the near future.

(ii) Electrolyte infiltration. The current rapid development of solid-state electrolytes and ionic liquid electrolytes has fully expanded the range of electrolyte options and satisfied the needs of electrolytes in different application scenarios. Particularly, solid-state electrolyte has obtained much popularity in the realm of MSCs manufacturing (Table 1) due to its capability of easy processing and no leakage issues of organic solvents. It has been considered as a promising electrolyte to improve the performance of MSCs. With the widespread application of nanotechnology, the interface problem of nanostructures has attracted much attention in recent years. However, many MSCs based on 3D scaffold utilize aqueous or liquid electrolytes for sufficiently electrolyte infiltration (Table 2) because complete infiltration of solid-state electrolyte into nanostructure-based MSCs still remains a challenge. To address this challenge, some advanced strategies are put forward from a physical and chemical point of view, including vacuum infiltration, hot pressing, electrodeposition and electrophoretic deposition of solid-state electrolytes. In this case, the mechanical robustness and chemical stability of electrodes (current collectors and active materials) should be considered before the filling process of electrolyte. As discussed above, the ALD technique is a potential solution to accomplish the fully infiltration of solid-state and ceramic electrolyte.

(iii) Advanced characterized techniques. Advanced MSCs emphasize the pursuit for accurately controlling of electrode properties during electrochemical operation process, and in-situ characterization techniques are expected as the promising methods, such as in-situ Raman spectroscopy and in-situ transmission electron microscopy. For MSCs, detailed information about the electrode properties is necessary to insight the evolution mechanisms of active materials and further understanding the detrimental effect of volume changes on nanostructures during the charging-discharging process of electrodes based on smart design. Hence, the developing of advanced characterized techniques is very practically necessary.

(iv) Advanced theoretical simulation and analysis. Advanced modeling is an essential complementary tool of characterization to insight the smart design contribution of high-performance electrodes. For instance, except for the overview of morphologies and structural changes of electrodes during the charging-discharging process of electrodes via characterization, theoretical simulation and analysis ensure a precise pertinence of smart optimization of electrode design for advanced MSCs. In addition, it offers further understanding of the active material utilization ratio and the appropriate optimization of parameters and morphologies of structured electrodes. Of note, advanced theoretical simulation and analysis also provide a reference of solid-state electrolyte infiltration situation via showing the electrolyte concentration gradients of the electrodes. In this context, the combination of characterization and modeling is an effective method to understand new emerging paradigm techniques such as rolling origami which possesses different features from the existing geometries. Considerable work should be devoted into developing modeling platform and the relevant research should attract more attention, which is significant for the next-generation smart design of electrodes for MSCs.

Finally, another important aspect is the integration compatibility of MSCs based on smart design of electrodes. For the rational application of MSCs, compatibility with the application environment is another essential issue and should be considered. For example, nBSCs utilized in miniaturized intravascular implants for medical treatment should be compatible to the hemodynamic conditions of the vascular system. In blood flow, nBSCs should possess stable performance without gas evolution during the operation and durable mechanical property to withstand various physiological conditions in vessels. Owing to similar challenges exist for both MSCs and MBs electrodes, ideas are borrowed from the leading-edge MBs to review the recent smart design of electrodes of high-performance MSCs to some extent. And the research and development of MBs have already been highly advanced in electrochemistry and microelectronic fields. Smart design of electrodes will pave the way to shorten the energy density gap between MSCs and MBs. We hope this review will attract more research attention on smart design strategies of electrodes. The smart design of electrodes reviewed in this article will inspire reasonable ideas for interdisciplinary researchers working in the fields of miniaturized device design for energy harvest, conversion, and storage as well as in the fields of material sciences, nanotechnology, and microelectronic device integration.
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CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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