

Substrate-Free and Shapeless Planar Micro-Supercapacitors

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Micro-supercapacitors (MSCs), albeit powerful, are unable to broaden their potential applications primarily because they are not as flexible and morphable as electronics. To address this problem, a universal strategy to fabricate substrate-free, ultrathin, shapeless planar-MSCs with high-performance tenability under serious deformation is put forward. These represent a new class of “all-inside-one” film supercapacitors, achieved by encapsulating two-dimensional interdigital microelectrodes within chemically cross-linked polyvinyl-alcohol-based hydrogel electrolyte containing graphene oxide (GO). GO nanosheets significantly improve ionic conductivity, enhance the capacitance, and boost robustness of hydrogel electrolyte. Consequently, the entire MSC, while being only 37 μm thick, can be crumpled and its shape can self-adjust through fluid channel ten times smaller than its original size without any damage, demonstrating shapelessness. Using MXene as active material, high single-cell areal capacitance of 40.8 mF cm^{-2} is achieved from microelectrodes as thin as 5 μm . Furthermore, to demonstrate wide applicability of this protocol, screen-printed graphene-based highly integrated MSCs connecting nine cells in series are fabricated to stably output a high voltage of 7.2 V while crumpling them from 0.11 to 0.01 cm^{-3} , manifesting superior performance uniformity. This protocol allows the coexistence of high performance with incredible flexibility that may greatly diversify MSCs' applications.

1. Introduction

Electrochemical energy storage devices (EESDs) are presently at the frontier of clean energy research. However, they have

not been able to keep up with the rapid progress in energy generation and consumption devices due to constraints on form factor of the EESDs. Form factor is an aspect of device design that defines and dictates the shape, size, and other physical specifications of components, especially in consumer electronics and electronic packaging. On the scale of large devices, EESDs are too bulky to perform at an optimal level due to various factors concerning components from the electrodes and electrolyte materials to supporting substrates and packaging materials involved. On the microscopic scale, only limited form factor is available depending on substrate flexibility, which significantly hinders the integration of EESDs into microelectronics and microsystems. Even today, micro/nanorobots have limited applicability because they rely on either biological functions or magnetic fields for locomotion, due to a lack of an integrable power source.^[1] To this end, great attempts have been devoted to create flexible or stretchable EESDs, such as buckled carbon nanotube-based supercapacitors, self-similar serpentine structured bat-

teries, and stretchable supercapacitors on rubber substrates.^[2–4] However, the presence of substrate or complex packaging materials involved ultimately increases the overall thickness of device, and reduces the chance of micro or nanoscale integration by compromising flexibility. So far, the studies on ultrathin EESDs, e.g., interdigital planar micro-supercapacitors (MSCs),^[5–8] have mostly dealt with ultrathin nanosheets or films as active materials while the whole device is usually supported on thick polymer substrates (typically, thickness of hundreds of micrometers),^[9] like polyethylene terephthalate (PET), and encapsulated by thick packaging materials. Therefore, the limited flexibility and large volume of the entire device usually overshadows the high electrochemical performance and intrinsic flexibility of the used active materials and electrodes that are only tens of nanometers to a few micrometers in thickness, while the overall thickness of the device including substrate and packaging is about several hundreds of micrometers thick or more.^[10]

Judging by the above criteria for creating versatile EESDs with high performance and variable form factors, we need to not only consider electrodes as a parameter but also take electrolyte into account. Hydrogel-based aqueous electrolytes have revolutionized the sector of quasi-solid-state supercapacitors. Synthetic hydrogel-based aqueous electrolytes not only provide

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designable mechanical flexibility without liquid leakage but also offer additional safety by maintaining fixed distance between electrodes to avoid short-circuits. Unfortunately, to the best of our knowledge, hydrogel-based aqueous electrolytes have mostly benefited sandwich-like stacked supercapacitors,^[11–15] but remain unexplored for ultrathin planar interdigital MSCs with form factors. Such MSCs can potentially add more functional features to the existing scope of interdigital MSCs and help us realize further new-concept electronic devices that will not be hindered by form factors of energy storage units. To envision a leap in functionality, planar MSCs should not only be ultraflexible and ultrathin but also pack a high amount of energy, which can be achieved by using high capacitance 2D active materials for microelectrodes such as graphene and MXene.^[16–19]

Sandwich-like stacked and fiber-based supercapacitors have demonstrated some incredible feats of flexibility, e.g., folding, looping, and stretching.^[20] However, planar interdigital MSCs are technologically more viable for integrating and powering microscale electronics on the same substrate,^[21] but sandwich-like supercapacitors are limited in such applications due to the unmatched device geometry. Fiber-based supercapacitors are marred with problems like component compatibility, complicated electrode preparation, nonscalability, and incompatibility with microelectronics manufacture.^[22–24]

The need of the hour is a way to create new-concept ultrathin planar MSCs so that the shape of microelectrodes, nature of electrolyte, substrate, etc., do not dictate the overall form factor of the device. Therefore, developing ultrathin MSCs with no restrictions on form factors and easily integrable with microelectronics is urgently required to close the gap between MSCs and microelectronics. To achieve this purpose, we herein report a facile, versatile, and scalable technique to realize substrate-free, ultrathin, shapeless MSCs (denoted as SMSCs) by encapsulation of flat MXene based interdigital microelectrodes in graphene oxide (GO) incorporated chemically crosslinked polyvinyl alcohol (PVA) aqueous hydrogel electrolyte (GPAH) thin film, showing ultrathin overall device thickness of as low as 37 μm , and high single cell areal capacitance of $\approx 40.8 \text{ mF cm}^{-2}$. Notably, the interdigital SMSCs do not display any significant change in performance even upon extreme deformation, demonstrative of shapeless characteristic. Even under zero-maintenance conditions, such SMSCs can function perfectly without affecting the electrode microstructure, evidencing the advantages of encapsulating interdigital electrodes within a thin film of electrolyte. Moreover, the highly integrated SMSCs (denoted as SPG-SMSCs) fabricated by screen-printed graphene (SPG) as microelectrodes and interconnects display exceptional performance uniformity and unprecedented flexibility, demonstrative of outstanding scalability and practicality of this protocol.

2. Results and Discussion

2.1. Fabrication of SMSCs

The schematic of fabrication of ultrathin planar SMSCs is illustrated in **Figure 1a**. First, a dispersion of MXene

with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (1:1 ratio by weight) was prepared by mild ultrasonication. Ultrathin MXene nanosheets with lateral size of 1–3 μm as seen in the corresponding transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were obtained by LiF/HCl etching (Figure 1b,c).^[5] Raman spectrum showed the characteristic peaks of MXene at 200, 400, 600, and 723 cm^{-1} (Figure 1d), without any signal of titanium oxide, suggestive of high-quality unoxidized MXene. Second, interdigital microelectrodes of MXene/PEDOT (denote as MP) were prepared on cellulose filter paper by mask-assisted vacuum filtration,^[25] followed by filtration of 0.5 M H_2SO_4 solution. The rationale for using PEDOT:PSS is to impart flexibility to the brittle MXene microelectrodes without compromising conductivity. H_2SO_4 treatment would accelerate the crosslinking of PEDOT and aid the dissolution of PSS phase,^[4] resulting in enhanced conductivity (42 S cm^{-1}) and greatly improved mechanical strength of microelectrodes compared to those without acid treatment (35 S cm^{-1}). Afterward, an ultrathin ($\approx 8 \mu\text{m}$) layer of water-soluble PVA was deposited on a PET sheet that served as the temporary substrate for subsequent crosslinking with the GPAH electrolyte deposited on it. Raman spectra of GPAH (Figure 1d) showed the characteristic G peak close to 1580 cm^{-1} , and indistinguishable D peak due to the presence of PVA. After sufficient drying of the GPAH, the as-prepared interdigital MP microelectrodes were directly transferred onto this GPAH/PVA/PET layer by dry stamping. Finally, a second layer of GPAH was deposited on top of the MP microelectrodes and allowed to dry for $\approx 4 \text{ h}$ under vacuum condition. When it was sufficiently dried, the all-in-one integrated film of GPAH/MP/GPAH could be easily peeled off from the PET sheet to obtain the freestanding, substrate-free MP-based SMSCs (denoted as MP-SMSCs). It is worth noting that, by optimizing the concentration and volume of MXene-PEDOT (e.g., 0.1 mg mL^{-1} , 2 mL), ultrathin microelectrodes, with thickness as low as 3 μm (Figure 1e), were fabricated. The unique device architecture allowed such ultrathin electrodes to be unaffected by extreme deformation. Cross-sectional scanning electron microscopy (SEM) images (Figure 1f,g) clearly exhibited the layered structure of MP film encapsulated by the GPAH electrolyte, giving a total device thickness of $\approx 37 \mu\text{m}$. This could be made thicker or thinner by varying the amount of GPAH, which can efficiently balance the trade-off between mechanical properties and electrochemical performance of MP-SMSCs.

2.2. Electrochemical Performance of MP-SMSCs

To demonstrate the excellent electrochemical performance of substrate-free and ultrathin MP-SMSCs, we first carried out cyclic voltammetry (CV) at different scan rates from 4 to 100 mV s^{-1} and galvanostatic charge and discharge (GCD) profiles at various current densities from 0.16 to 0.80 mA cm^{-2} (Figure 2a,b), with MP mass loading of 0.8 mg cm^{-2} . Good capacitive behavior was evident from the retention of quasi-rectangular shape of CV curve even at high scan rate of 100 mV s^{-1} as well as nearly symmetric triangular GCD profiles. The specific areal capacitance of a cell measured at 0.16 mA cm^{-2} was calculated to be 40.8 mF cm^{-2} which is higher than those of the

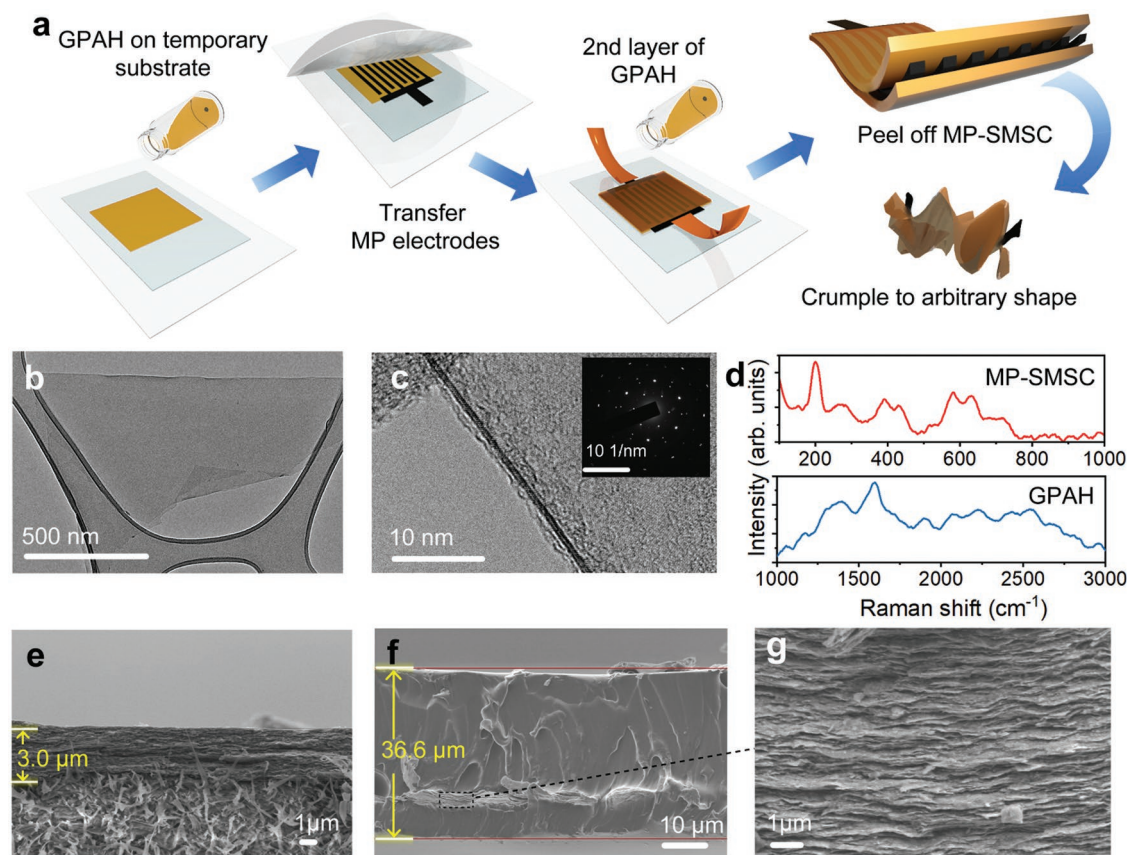


Figure 1. Fabrication of SMSCs and materials characterization. a) Schematic showing the fabrication of MP-SMSCs. b,c) TEM and HRTEM images of 2D MXene nanosheets. Inset shows the selected area electron diffraction pattern. d) Raman spectra of MP thin film used as microelectrodes and GPAH used as electrolyte. e) Cross-section SEM image of MP microelectrode with a typical thickness of 3 μm . f) Cross-section SEM image of a complete, optimized ultrathin MP-SMSC, with a total device thickness of $\approx 36.6 \mu\text{m}$. g) Magnified view of SEM image of MP microelectrode cross section.

reported MXene-based MSCs using aqueous gel electrolytes, like stamped (28.3 mF cm^{-2} at 5 mV s^{-1}), spray-coated or sandwiched MXene based MSCs on paper (25 mF cm^{-2} at 20 mV s^{-1}), thick PET (22.4 mF cm^{-2} at 0.25 mA cm^{-2}), or glass (27.3 mF cm^{-2} at 20 mV s^{-1}) substrates (Table S1, Supporting Information).^[10,26–29] Furthermore, during long-term GCD tests, the charge–discharge times were nearly equal, indicative of high Coulombic efficiency close to 100%. Figure 2c shows the rate capability of MP-SMSCs. Notably, $\approx 75\%$ of the initial capacitance was retained when current density was increased fivefold from 160 to $800 \mu\text{A cm}^{-2}$, suggestive of exceptional rate capability due to high electrical conductivity of MP microelectrodes, intimate contact of electrolyte with electrode and efficient transport of ions through the hydrogel matrix. The Ragone plot shown in Figure 2f demonstrates high areal energy density of $2 \mu\text{Wh cm}^{-2}$ at 0.06 mW cm^{-2} and maintains $1.5 \mu\text{Wh cm}^{-2}$ at 0.25 mW cm^{-2} , which will allow SMSCs to be of widespread interest in diverse flexible electronics. It is noted that by increasing the thickness of electrodes ($12 \mu\text{m}$) our protocol offers a very high areal specific capacitance of 161 mF cm^{-2} per cell measured at 0.2 mA cm^{-2} (644 mF cm^{-2} based on single electrode), which is among the highest reported value from conventional MXene based MSCs (Figure S4, Supporting Information). However, such thick

electrodes show limited flexibility and are not sustainable under extreme deformation. Additionally, with no substrate blocking the bottom surface (e.g., for conventional planar MSCs on a substrate), the flow of electrolyte ions could be unhindered. This in principle should significantly improve the capacitance, especially, at high rates, because of enhanced ion diffusion, as we demonstrated in our previous work about the presence of multiple ionic diffusion pathway in the planar MSCs.^[30]

2.3. Role of GO in SMSCs

In our work, we used GO as an additive to the hydrogel electrolyte, first, to solve the key problem of rapid water evaporation and to promote water retention over long time (without packaging),^[31,32] and second, to enhance capacitance and rate performance by improving ionic conductivity. To elucidate the important role of GO on the mechanical and electrochemical performance of our MP-SMSCs, we also fabricated GO-free PVA hydrogel electrolyte for comparison, while other steps were kept unchanged. Previously, GO incorporated PVA-based hydrogels have been prepared by physical cross-linking (e.g., freeze–thaw cycles),^[33–35] which is not a reliable approach for scaling up supercapacitors and requires high amount of energy to process.

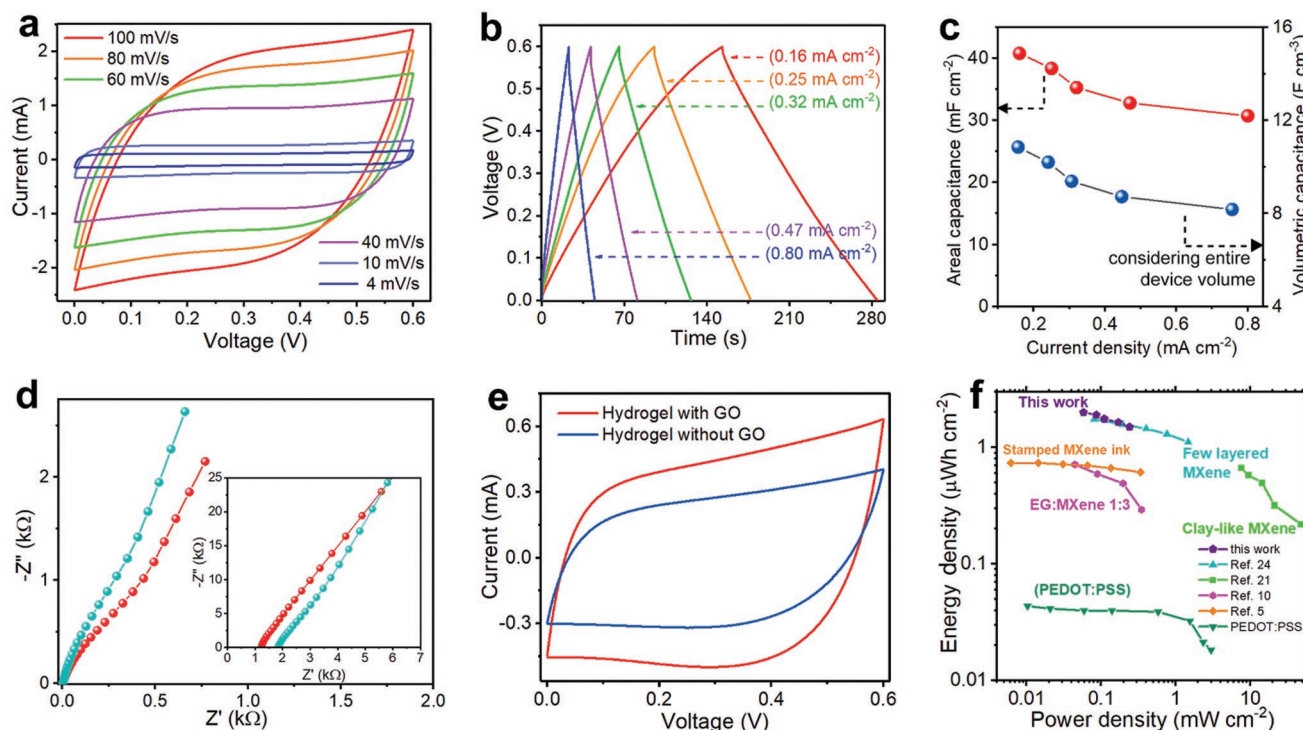


Figure 2. Electrochemical characterization of MP-SMSCs. a) CV curves of MP-SMSCs tested at different scan rates from 4 to 100 mV s⁻¹. b) GCD profiles of MP-SMSCs obtained at different current densities. c) Areal capacitance as a function of current density. d) Nyquist plots of PVA hydrogel electrolytes with and without GO incorporation. e) CV curves of MP-SMSCs showing the effect of GO incorporation into PVA hydrogel electrolyte. f) Ragone plot comparing performance of MP-SMSCs with other MXene-based MSCs.

In our case the GPAH electrolytes, prepared by incorporating GO during chemical cross-linking process, possessed three roles, including ultrathin ionic conductor, capacitance enhancer, and water retention. The significant improvement in ionic diffusion was observed from the Nyquist plots for hydrogel electrolyte with and without GO (Figure 2d). Analyzing the Nyquist plots, the slope of low-frequency tail indicated the electrolyte diffusion resistance into the electrode. In both cases, the slope is equal due to the fact that stainless steel was used as the blocking electrode to solely characterize the electrochemical properties of the electrolytes and avoid any interference from active materials. The high-frequency quasi-semicircle mainly represents the bulk ionic resistance of the electrolyte, i.e., the bigger the intercept of the apparent semicircle, the larger the resistance.^[36] It is clear from the apparent smaller semicircle size in case of GPAH that the bulk resistance is low, facilitated by the excellent ionic conductivity of GO. Furthermore, the equivalent series resistance in GPAH is slightly lower than the one without GO. As demonstrated, the addition of GO led to a significant increase in the area under CV curves of MP-SMSCs with equal mass loading, suggestive of an enhancement in the cell's areal capacitance from 7.29 to 12.1 mF cm⁻², nearly 66% increase (Figure 2e). Notably, GO exhibited the positive effects on greater water retention due to the presence of functional groups on its large surface area elucidated by significantly enhanced cycling stability (Figure S1, Supporting Information).^[31] Compared with GO-free devices, MP-SMSCs with GO incorporation showed obvious flexibility and resistance to mechanical damage under extreme deformation after long-time exposure to ambient

conditions and freeze-drying (Figure S2, Supporting Information). GO incorporation into elastomers could greatly enhance mechanical properties by virtue of hydrogen bonding,^[37] which is very important for improving the robustness of GPAH. GO incorporated MP-SMSCs, operated without any packaging, showed as high as 100% capacitance retention after 300 cycles while device without GO retained only 50% of their initial capacitance under the same conditions (Figure S1a, Supporting Information), demonstrative of GO's uniqueness in water retention properties. With proper packaging in a crumpled state using organosilicone, our MP-SMSCs showed high capacitance retention of 75% after 10 000 cycles comparable with reported literatures (Figure S1b, Supporting Information).^[10,27–29] However, the cycling stability of MP-SMSCs is sensitive to environmental conditions, the concentration of GO, and the electrolyte used (Figure S1c,d, Supporting Information) resulting from the oxidation of MXene.^[29] Surprisingly, even after freeze-drying SMSCs for 6 d, SMSCs with GPAH electrolyte could retain flexibility and showed no visible change in their electrochemical performance (Figure S2, Supporting Information), suggesting that our SMSCs can be stored for a long time without packaging in low temperature condition.

2.4. Advantages of Hydrogel Electrolyte

We achieved the encapsulation of ultrathin interdigital micro-electrodes inside a hydrogel electrolyte for substrate-free planar SMSCs by using a stepwise alternate gel deposition and

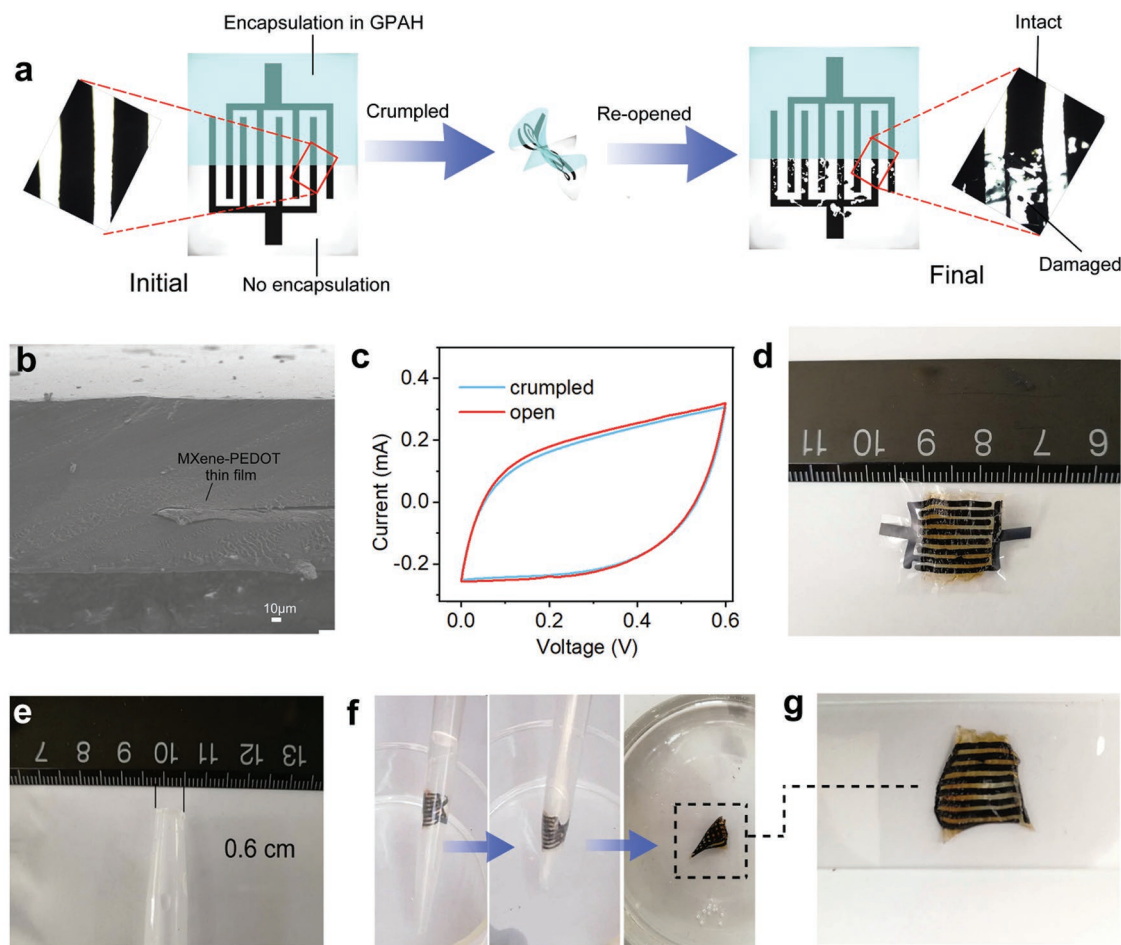


Figure 3. Shapeless feature and characterizations of MP-SMSCs. a) Photographs and schematic showing the protective effect of hydrogel electrolyte encapsulation on a section of microelectrodes under extreme deformation compared to an unencapsulated region. b) Cross-section SEM image of MP-SMSCs showing the encapsulation of ultrathin MP microelectrodes in electrolyte hydrogel. c) Performance of MP-SMSCs under crumpling deformation. d,e) Photograph showing dimensions of a typical MP-SMSC and the nozzle used. f) Photographs taken during the ejection of MP-SMSCs through the nozzle. g) Ejected MP-SMSCs reopened to show no damage to the microelectrodes.

chemical cross-linking, which has not been reported so far. There are numerous advantages in merit of this architecture. First, being encapsulated in hydrogel electrolyte the interdigital microelectrodes were well protected against mechanical faults. **Figure 3a** shows optical image of a section of MP-SMSCs. It is clearly seen that after multiple series of extreme deformations like crumpling, stretching, and rolling, the region that was not encapsulated suffered from large cracks while the region encapsulated within the hydrogel electrolyte exhibited no obvious structural breakage. For further verification of outstanding encapsulation, cross-sectional SEM images of MP-SMSCs with thicker hydrogel electrolyte ($\approx 178 \mu\text{m}$) were obtained (**Figure 3b**), clearly showing the successful encapsulation and intimate contact between the MP microelectrodes and GPAH electrolyte. A similar device was made by depositing hydrogel on MP microelectrodes stamped on ultrathin PET substrate ($\approx 12 \mu\text{m}$), without encapsulation, the microelectrodes showed serious structural failure under above-mentioned mechanical deformations (**Figure S3**, Supporting Information) due to the delamination of electrolyte hydrogel from PET

surface. Therefore, it is confirmed that the encapsulation could greatly protect MP microelectrodes by preventing delamination and maintaining configurational invariability of the microelectrodes in the hydrogel matrix. It should be mentioned that such substrate-free MP-SMSCs did not require the consideration of the different interfacial adhesion of electrode–substrate, electrolyte–substrate, packaging material–substrate, and so on. Therefore, our strategy can be universally applied to all kinds of active materials.

Second, for fabrication of highly conductive and continuous MP interdigital microelectrodes, a composite of MXene with PEDOT was prepared. PEDOT does not offer significant capacitance but it imparts a great benefit in terms of conferring mechanical flexibility and ease of stamp transfer onto hydrogel film while maintaining superior conductivity of microelectrodes.^[4] Filtering H_2SO_4 through the electrodes was essential in cross-linking the PEDOT to create an ultrathin but strong freestanding film.^[38] The cross-linking was evident from the observation that after the acid treatment it becomes very difficult to filter further fluid through the microelectrodes. Most

reports demonstrating the flexibility of planar MSCs only go as far as showing various bending states up to 180° or 0° folding radius. In principle, they are limited by the nature of electrolyte and the substrate. Since our SMSCs do not have a substrate and the all-inside-one film was mechanically robust hydrogel, the ultrathin substrate-free device was able to sustain extreme deformation without any significant loss of performance. As a proof of this concept, MP-SMSCs were deformed by arbitrary crumpling, and the corresponding CV curves before and after crumpling were measured (Figure 3c). Remarkably, it can be seen that the CV curve was nearly unaffected by the crumpling, evidencing the superior mechanical endurance and shapelessness of our device.

Third, since GPAH electrolyte itself was freestanding and ultraflexible, there was no need for a substrate. More importantly, it has a rubber-like texture which helps in reducing stress compared to plastic-like texture of thin PET sheets. This not only reduced the thickness of the overall device but also was important for rendering the device shapeless. To demonstrate the shapelessness of the device, one substrate-free MP-SMSC (Figure 3d) was loaded into a pipette with a mixture of ethanol and water. Then, the pressure was applied on one side to eject the solution along with MP-SMSC through a nozzle (diameter of 0.6 cm) (Figure 3e). Impressively, the substrate-free MP-SMSC was able to squeeze itself through the small nozzle of the pipette (Figure 3f), which was nearly ten times smaller than the lateral size of the device. The crumpled device was reopened to assess any damage to the microelectrodes and it was observed that they were intact (Figure 3g). This kind of feature is highly useful to reduce the volumetric footprint of energy storage devices drastically without compromising performance.

By removing substrate as a parameter, we witnessed an unprecedented freedom for multiple device integration and new architectures. The GPAH electrolyte also exhibited temporary spontaneous interface healing properties for a few hours after gelation.^[39] If the device is folded on itself during this period, then it retained remarkable electrochemical performance while healing the interface between the overlapped GPAH. This effectively means shorter transport paths for ions between different region of the microelectrodes. Intuitively, this may not be possible if there was a substrate blocking the free flow of ions. Additionally, using freestanding high-voltage GO-based ionogel electrolytes,^[40] the electrochemical performance and form factors of such substrate-free SMSCs could be further improved.

2.5. Scalable Fabrication of SPG-SMSCs

This protocol for encapsulating ultrathin electrodes into PVA-based hydrogel matrix can be applicably extended to different 2D materials and microelectrode fabrication methods. To demonstrate the scalability and universality, we also used screen-printing technique and graphene ink to prepare graphene-based shapeless SMSCs. This method for preparing SPG-SMSCs, as shown in Figure 4a, was quite similar to that for MP-SMSCs, in which the only difference was the deposition of microelectrodes on PVA film using screen printing instead of dry stamping transfer. Screen printing is an attractive method

for industrial-scale manufacture of planar MSCs because it is cheap, reliable, and has high throughput.^[41,42] Using screen printing technique, shapeless integrated SPG-SMSCs with arbitrary form factors were fabricated. From the CV curves and GCD profiles (Figure 4b–d), it is evident that SPG-SMSCs were able to operate normally at a wide range of scan rates and current densities. Furthermore, the CV profile of SPG-SMSCs even at an ultrahigh scan rate of 100 000 mV s^{−1} showed a quasi-rectangular shape. At 100 000 mV s^{−1}, it retained nearly 20% of its initial capacitance (Figure S6, Supporting Information), indicative of superior rate capability. Such remarkable rate capability in SMSCs is a result of high electrical conductivity of SPG films (36 S cm^{−1}) as active materials and metal-free interconnects simultaneously to eliminate interfacial resistance.^[43] With the help of screen printing, we were also able to print the integrated SPG-SMSCs by connecting three cells in series. Notably, the CV curves of corresponding one to three devices tested at 50 mV s^{−1} are shown in Figure 4e, which verified the increase in total voltage achievable from serially connected SMSCs. The GCD profiles (Figure 4f) also evidenced the stepwise increase in the output voltage available from 0.8 V for single cell to 2.4 V for three serially connected cells, demonstrative of outstanding performance uniformity. Because of this unique protocol an extra dimension of shapelessness was added to the outstanding performance of SPG-SMSCs to reduce the total footprint of energy storage device module.^[43] The serially connected SPG-SMSCs were able to easily power two liquid crystal displays (LCD) connected in parallel requiring at least 2.2 V to operate (Figure 4g) even under extreme mechanical deformation, holding great potential for powering electronics under inhospitable situations.

Not only the electrochemical performance but also just like MP-SMSCs, SPG-SMSCs demonstrated excellent physical resilience under strong mechanical deformations, such as crumpling, spiraling, and bending. To validate this formless feature of withstanding the arbitrary yet strong deformations, our integrated SPG-SMSCs were put through a series of such tests in a pristine state, a spirally deformed state, and an extremely rough deformed state (Figure 5a–c). To further witness its resilience, the SPG-SMSCs were put through 3000 cycles of extreme crumpling deformation. For crumpling it, we first folded the SPG-SMSCs along its longitudinal axis and then compressed it inwards from its endpoint. Remarkably, the device showed nearly 100% capacitance retention even after being subjected to crumpling 3000 cycles (Figure 5c). The slight increase in capacitance observed after the first 100 cycles was attributed to the interface healing of GPAH while folding over itself. This effectively increased the amount of electrolyte ions available in the vicinity of graphene microelectrodes. While reopening after each cycle of crumpling, the device was also given a minor stretch. The excellent performance retention despite this stretch may hint the application of this protocol for preparing stretchable interdigital SMSCs through further modification of the electrolyte and microelectrodes in the future.

Future applications of energy storage devices require form factors such as shape diversity for satisfying internet of things, scaling up for manufacturing multiple units conveniently, and seamless integration of these units to tailor the capacitance and voltage output. To this end, we further demonstrated

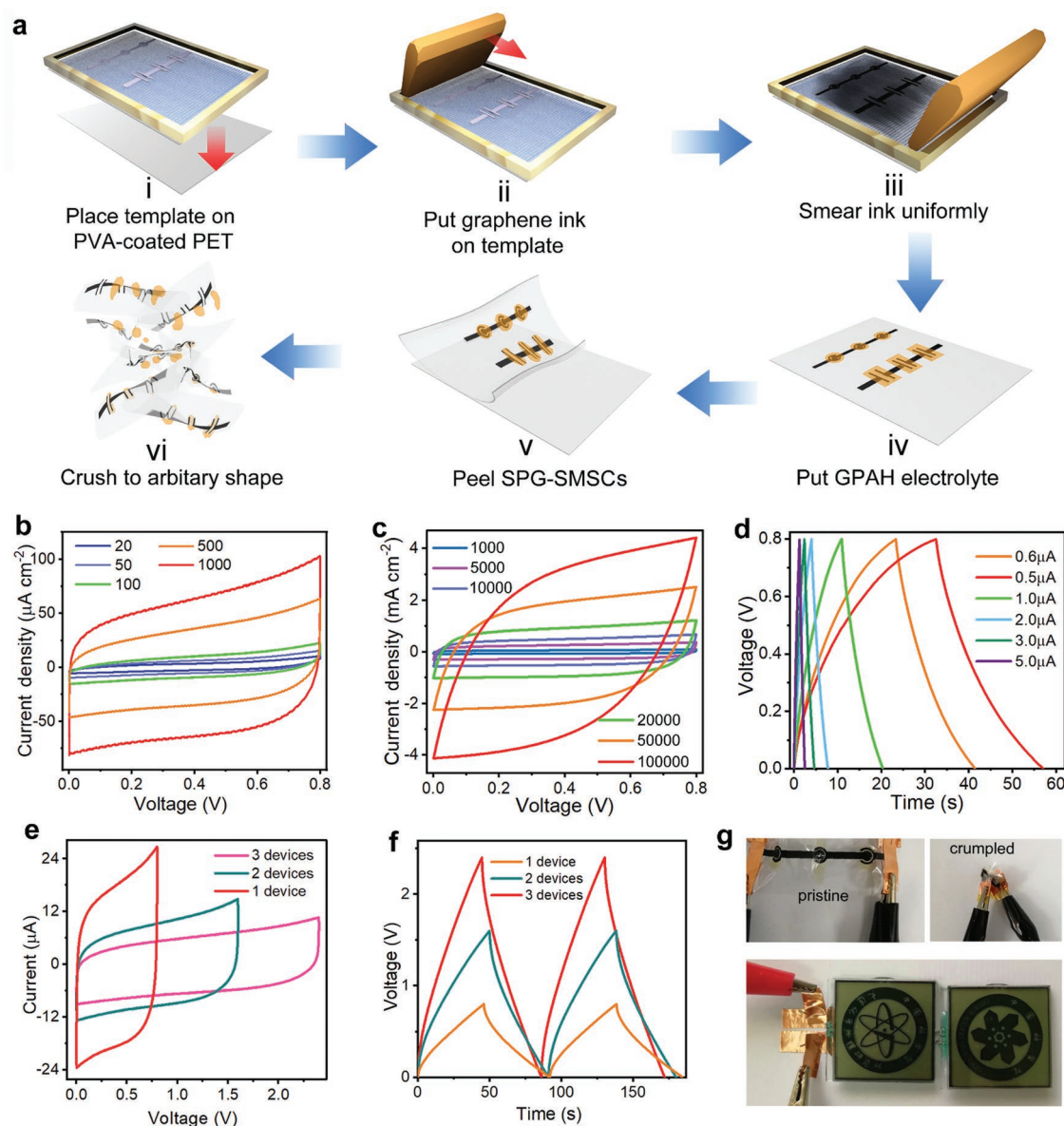


Figure 4. Fabrication and electrochemical performance of SPG-SMSCs. a) Schematic for fabricating SPG-SMSCs. b,c) CV curves obtained at different scan rates from 20 to 100 000 mV s^{-1} and d) GCD profiles from 0.5 to 5.0 μA for a single unit of SPG-SMSCs. e) CV curves of SPG-SMSCs connected in series fashion at a scan rate of 5000 mV s^{-1} . f) GCD profiles of three SPG-SMSCs connected in series, measured at 2 μA . g) Three serially connected SPG-SMSCs pack in flat and extremely crumpled state can power up two LCD screens connected in parallel.

the integration ability of SPG-SMSCs to be manufactured for high-voltage applications by connecting nine individual cells in series, using only graphene inks for microelectrodes, interconnects, and metal-free current collectors. As expected, the voltage scaled linearly from 0.8 V for a single SPG-SMSC to 7.2 V for nine serially connected SPG-SMSCs (Figure 5d). This integrated SPG-SMSCs pack demonstrated CV curves while being in a completely crumpled state with nearly rectangular shape even at a high scan rate of 1000 mV s^{-1} . This outstanding performance uniformity was also verified by GCD profiles which showed negligible ohmic drop operated at various current densities (Figure 5e). Additionally, to further verify the potential of SPG-SMSCs as a microscale power

source for nanorobotics, three serially connected SPG-SMSCs (3 cm $\times$ 1 cm) were crumpled and inserted into a tiny capsule (diameter of 0.5 cm, length of 1.5 cm) (Figure S7a, Supporting Information). Unsurprisingly, such SPG-SMSCs pack was able to function normally even under such stress and output a stable voltage of 2.4 V and could power two LCD screens simultaneously (Figure 5f). Further, eight serially connected SPG-SMSCs were crumpled and inserted into a medicine capsule. Under extreme crumpling deformation, this tiny setup (diameter of 1.5 cm, length of 2.5 cm) (Figure S7b, Supporting Information) showed stable CV curves up to a high scan rate of 100 000 mV s^{-1} with a high voltage output of 6.4 V (Figure 5g), capable enough to power multiple nanoscale electronic devices

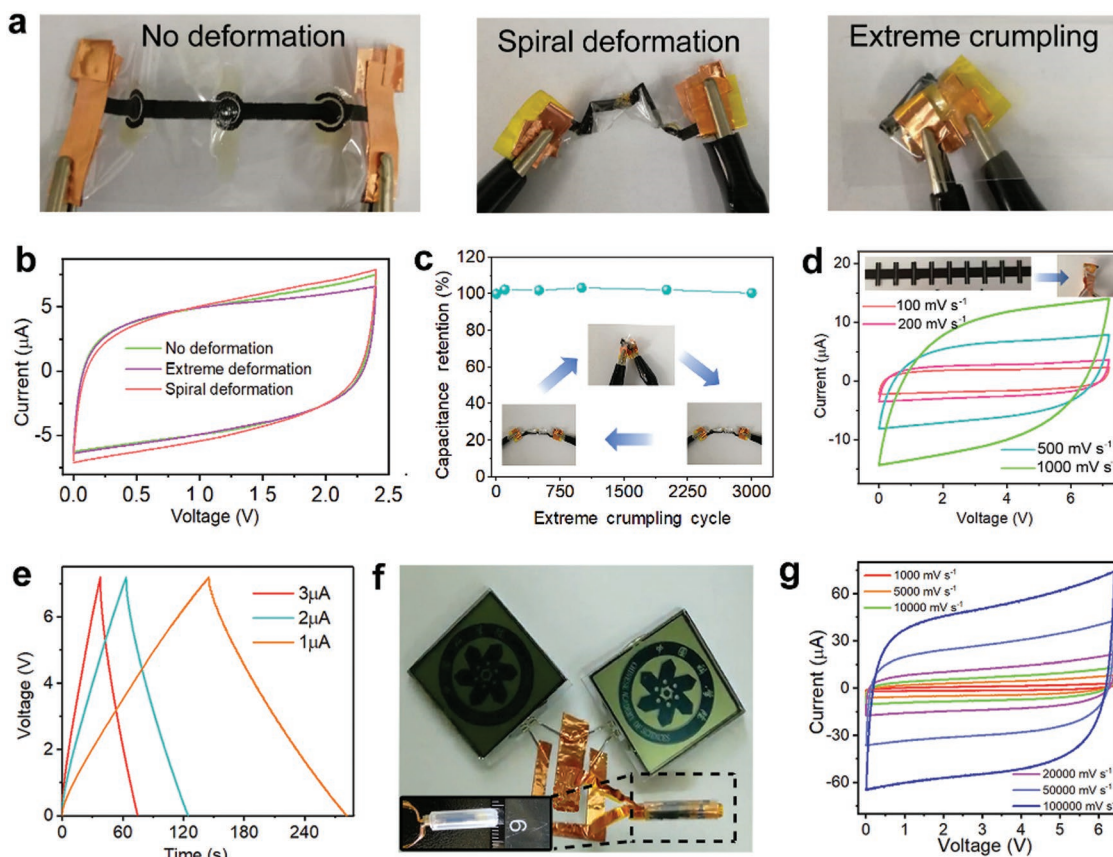


Figure 5. Shapeless feature and electrochemical performance of integrated SPG-SMSCs. a) Photographs showing the different deformation states of SPG-SMSCs. b) CV curves of SPG-SMSCs obtained under different deformation states. c) Capacitance retention as a function of extreme crumpling cycles. d,e) CV curves tested at different scan rates from 100 to 1000 mV s^{-1} , and GCD profiles at different current densities of nine series-connected SPG-SMSCs pack crumpled to a very small size. f) Three serially connected SPG-SMSCs in a capsule powering two LCD screens. Inset: Photograph of three serially connected SPG-SMSCs extremely crumpled and inserted into a capsule (diameter of 0.5 cm, length of 1.5 cm). g) The stable CV curves of eight serially connected SPG-SMSCs pack crumpled and inserted into a medicine capsule and tested at different scan rates from 1000 to 100 000 mV s^{-1} .

in different media for variety of applications (Figure S7c,d, Supporting Information).

It is worth noting that our SMSCs can not only find a place in conventional applications but also provide a facile solution for some complicated, future unconventional applications of supercapacitors. This is substantiated by the insertion of the SMSCs into easily ingestible capsules that may be useful for biomedical applications, like self-powered remotely guided microrobots (Figure 5f). Moreover, the ability of SMSCs to morph their shape according to the environmental forces (Figure 3f) opens up future applications for shape-shifting robotics, swimmer drones. Further, ultraflexible electronics have been realized for meeting future applications, such as artificial skin^[44] and ultrathin integrated electronic devices,^[45] but a gap exists in the solutions available for integrating them with energy storage devices. The removal of substrate renders the SMSCs ultrathin, and the unique architecture achieved by encapsulating 2D electrodes in a thin film hydrogel electrolyte makes them mechanically robust, demonstrative of an ideal candidate for integration with next-generation electronic systems.

3. Conclusion

In summary, we have demonstrated the facile fabrication of substrate-free, formless and ultrathin planar SMSCs fabricated by encapsulating MXene or graphene-based microelectrodes inside GPAH electrolyte. These new-concept SMSCs showed electrochemical performance at par with traditional MXene-based MSCs in interdigital patterns and surpassed the mechanical performance of previously reported MSCs by evidencing very little change in electrochemical performance despite extremely rough deformations. As demonstrated, the concept of shapeless SMSCs will be useful in future for building shape-shifting smart systems with broad variety of applications including military reconnaissance, nanorobotics, body implants, or targeted drug delivery assisted by nanorobots. Also, in future this strategy could possibly be modified to create dynamic EESDs with self-locomotive abilities. This facile, universal, tailorable, and inexpensive strategy would push the boundaries of EESDs to an extent where they are independent of substrate limitations. Therefore, such substrate-free and formless SMSCs, with further optimization of integration and miniaturization,

will also be used for efficient and large-scale manufacture of self-powered tiny nano/microrobots and other microsystems with integrated circuits to perform various tasks autonomously.

4. Experimental Section

Preparation of MXene: $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was synthesized from Ti_3AlC_2 by LiF/HCl etchants previously reported.^[5,46,47] Typically, LiF (0.5 g) was dissolved into 9 M HCl (10 mL) under stirring. Subsequently, Ti_3AlC_2 (0.5 g) was added slowly into the above solution with continuous stirring. The resultant mixture was stirred at 35 °C for 24 h. Subsequently, the etched product was washed with deionized water through centrifugation (3500 rpm, 5 min) several times until pH reached up to 6 and multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ sediment was obtained. Afterward, the obtained sediment was mixed with deionized water (10 mL) and the resulting mixture was subjected to vigorous shaking using vortex machine. Successively, the obtained dispersion was centrifuged multiple times to obtain the sediments. Finally, the resultant sediment was redispersed in deionized water under a vigorous shaking, with a concentration of 0.1 mg mL⁻¹, for further usage.

Preparation of GPAH Electrolyte: GPAH with low viscosity solution of 100 mg mL⁻¹ was prepared by mixing 2 mL GO (6.0 mg mL⁻¹) in 100 mg mL⁻¹ PVA solution under mild stirring at 90 °C until a homogenous solution was obtained. Then, 5 g of concentrated sulfuric acid (H_2SO_4) was added to the above solution while cooling down. Next, 2 mL of this solution was taken in a bottle and 20 μL of glutaraldehyde was mixed under constant stirring at room temperature to obtain a viscous solution within 30 s. Note that the gelation process took ≈ 10 min to complete, therefore this solution must be processed within 10 min.

Device Assembly: A very thin layer of low viscosity, water-soluble PVA (100 mg mL⁻¹) was smeared on thick PET sheet and heated at 55 °C. After heating for a few minutes, it formed a thin film that adhered to the PET sheet. While GPAH electrolyte was still fluid it was poured as a thin film on top of the dried PVA film. Interdigital MP microelectrodes of MP-SMSCs were fabricated from a composite of MXene and PEDOT:PSS with a mass ratio of 1:1. PEDOT:PSS was mixed dropwise with diluted MXene solution under mild stirring and ambient atmosphere. The mixture was then filtered through cellulose-based membrane (pore size of 0.45 μm) using mask-assisted vacuum filtration setup,^[48] followed by filtration of 0.5 M H_2SO_4 through the interdigital microelectrodes. Then, the as-obtained interdigital microelectrodes on filter membrane were allowed to dry for 30 min under vacuum conditions. The interdigital MP fingers were then easily transferred from filter membrane onto the GPAH thin film electrolyte by dry stamping. After gelation was complete, the prepared interdigital microelectrodes were stamped onto this assembly such that only the fingers of microelectrodes were on top of the electrolyte. Finally, another thin layer of GPAH electrolyte was deposited on the fingers by blade coating, and left to complete gelation for 10 min. After 30 min, the gel electrolyte underwent sufficient drying to form a robust layer assembly, which finally was peeled off from the PET sheet to obtain MP-SMSCs.

SPG-SMSCs were fabricated using the similar procedure of MP-SMSCs except the manufacturing method of microelectrodes and active materials. In this case, the screen printing was used for the preparation of graphene microelectrodes for SPG-SMSCs, as reported previously in a work.^[43] Subsequently, a thin layer of GPAH was deposited on the active area and allowed to dry. Finally, the whole SPG-SMSCs or integrated SPG-SMSCs were easily peeled off from the substrate.

Materials Characterizations: Materials characterization was conducted by SEM (JEOL JSM-7800F), TEM and HRTEM (JEM-2100), and Raman spectroscopy (LabRAM HR 800 Raman spectrometer, 532 nm).

Electrochemical Measurement: The electrochemical performance of the supercapacitors was evaluated by CV measurements at different scan rates, GCD profiles conducted at different current densities, and electrochemical impedance spectroscopy recorded in the frequency range from 0.01 Hz to 100 kHz with a 5 mV alternating current amplitude, using an electrochemical workstation (CHI 760E).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

graphene, micro-supercapacitors, MXene, shapeless, substrate-free

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