Recent Development of Integrated Systems of Micro-supercapacitors

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Abstract
Development of wearable and portable electronics promotes the miniaturization of energy storage devices. Micro-supercapacitor (MSC) featuring in fast charging and discharging rates, long cycle life and high-power density stands out from miniaturized energy storage devices, particularly for its small size and adjustable structure which is easily processed to integrate with other on-chip electronics. In this review, we systematically analyzed the MSCs integration with other electronics from the perspective of structures and functions. At the beginning, we briefly introduced typical MSCs with unique properties. Subsequently, applications and integrations of MSCs with energy-consuming or energy-generating electronics were highlighted. Furthermore, compatible materials and designed structure of the all-in-one device were also depicted. Finally, challenges and future development of MSCs integrated systems were put forward.

Key words
Integrated energy storage device; Micro-supercapacitor; All-in-one system; On-chip electronics; Miniature integrated circuits

1. Introduction
Recently, portable electronic and/or circuits of the devices with low power consumption, such as sensors, microprocessors and wireless communicating chips, tend to be miniaturized and integrated, which are increasingly powered by miniature electronic devices [1]. Among various micro-energy-supplying devices [2, 3], micro-supercapacitors have attracted extensive attention due to their small size, high power density, long cycle life, and fast charge-discharge rate [4-7]. Similar with the traditional supercapacitors, there are also two main energy storage mechanisms of MSCs: electrical double-layer capacitors and pseudocapacitors [8]. The former stores energy through the electrostatic attraction between the ions at the surface of the electrolyte and electrodes to generate electrical double layers. The latter is based on the fast-reversible surface redox reaction or the Faraday charge transfer reaction generated by the active materials at the interface between the electrolyte and electrodes [9]. Generally, both mechanisms may exist simultaneously [10]. Interestingly, different from the sandwich assembly of traditional energy storage electrodes
that requiring a separator to avoid short circuit between electrodes [11], MSCs usually present planar structures, and the two electrodes are separated in plane without additional separator. The narrow electrode gap of MSC allows rapid transportation of electrolyte ions between the electrodes. Due to the short diffusion distance, charges are easy to be accumulated and released during charging and discharging procedure, enabling an ultrahigh power density of MSC for electrical appliances. In addition, MSC is considered to be one of the most promising energy storage devices in wearable electronic devices [11, 12]. On the one hand, apart from the outstanding electrochemical properties, MSCs with specific functions including foldability [13-15], stretchability [16-20], and biocompatibility [11, 21] have been widely explored and applied into special occasions. For example, stretchable MSC can be attached onto stretchable surfaces as sensing skin to detect certain physiological activities [22-24]. On the other hand, the planar feature of MSC contributes to a thin integrated device which is feasible to be placed on the substrate. Additionally, the area of MSCs is usually within centimeters to millimeters and even micrometers scale, and they can be assembled in some portable electronic devices, such as integrated circuits on chips, micro robots and position indicators. More importantly, the integration of MSCs and other electronics gradually become critical development directions of MSCs, and constitute an important part of future integrated circuits. The integrated application of MSCs mainly involves the connections and matching degree between each electrical component, and the fitness of the materials and structures of the device. These discussions of the device have never been mentioned in some previous reviews on MSCs [25-27]. Herein, as shown in Scheme 1, this review introduces some special properties of multi-functional MSCs. From the perspective of integration, as the energy storage units, MSCs combining with energy-consuming devices (such as sensors) or energy-supplying devices are systematically discussed. To acquire a robust and compact structure, designing MSCs and various electronics into an all-in-one structure by using compatible materials is also listed. Finally, challenges and potential development of MSCs integrated systems are put forward.

Scheme 1 Brief introduction of micro-supercapacitors integrated system.
2. Multifunctional micro-supercapacitors

With the in-depth research, the MSCs with specific multiple functionalities, such as foldability [13-15], stretchability [16-20], biocompatibility [11, 21], waterproofing and so on, have attracted more and more attention in special-purpose occasions. Studies have shown that flexible and foldable MSCs could present controllable energy output through changing the folding [14, 15, 28-31]. For example, Fu [32] obtained an asymmetric paper-based MSC on cellulose paper with a voltage as high as 1.5 V by means of origami, and the surface capacitance value reached to 8.6 mF cm\(^{-2}\) (Figure 1(a-c)), which ingeniously utilized the foldability of the paper. By a similar folding method, Qu [29] imprinted graphene/polypyrrole composite foam into the paper substrate to fabricate the MSC electrodes array. The array realized series-/parallel-connection between MSCs through three different ways by folding paper, thereby adjusting the energy output.

Transparent MSC is also a special energy device, which can be used in electronic devices that requiring high light transmittance [33, 34]. Li [35] adopted ink-printing and dry-etching method to fabricate a scalable, thick-controllable, and transparent MSC (Figure 1(d)) with printed graphene flake film. Owing to the controllable printed layers of graphene flake, the transmittance of graphene electrode is adjustable. The highest transparency is up to 90% at 550 nm when the sheet resistance is 80 kΩ/sq. In addition, self-healing MSC has a high durability in practical applications which can recover from a complete fracture to its original state. Gao [36] introduced a self-healing polyurethane (PU) shell structure coating on the MXene and reduced graphene oxide (rGO) aerogel to obtain a self-healing MSC (Figure 1(e)). The self-healing property originates from abundant interfacial hydrogen bonds in the supramolecular network of carboxylated PU. After five times of shear healing, the MSC maintained 81.7% of the original capacitance performance, showing excellent self-healing ability. Since the MSCs with planar structure are inevitably pulled during practical applications, the concept of stretchable micro-supercapacitors has been proposed [17-19, 37, 38]. Ha [16] used Ecoflex as an elastic substrate to prepare Mn₃O₄/multi-walled carbon nanotube MSC electrodes by photolithography and layer-by-layer assembly techniques. The fabricated MSC could be stretched by 30% of length without any damage. This is because the tensile ratio of the carbon nanotube composite electrode is small, and the shared tensile strength is mainly applied on the Ecoflex elastic substrate and encapsulating materials, lessening the force on the electrodes (Figure 1(f)). Meanwhile, considering the hydrophobicity of Ecoflex, they improved the stretchable MSCs with the same tensile strength and water resistance (Figure 1(g)) [39]. These waterproof materials protected the structure of MSCs well, and guaranteed the normal work of MSCs under water to power LED lights.

In addition, exploration of biodegradable and environmentally friendly materials for MSCs is one of the important directions for development of safe and nontoxic micro power supplies in vivo [40-44]. Lee [21] successfully prepared a biodegradable MSC by using metal electrodes (e.g., Mo, W, and Fe) on poly(lactic-co-glycolic acid) substrate obtained by electron beam evaporation deposition, and NaCl/agarose gel as electrolyte. It can be completely degraded after placing the assembled MSC in phosphate buffer solution for few hours (Figure 1(h)). Edibility is a unique concept compared to biodegradability. Gao [45] replaced all the materials (including electrodes, substrates, electrolytes) of MSCs with edible materials made from daily food and built a directly swallowable edible MSC (Figure 1(i)). After being eaten by the tester, there was no abnormal reactions verifying the edibility of the MSC.
Figure 1 (a) A series of positive and negative electrodes were prepared on the same sheet, and the two electrodes in the middle were connected by silver nanowire (Ag-NW) wiring. (b) Folding the paper substrate to form the pack containing two tandem asymmetric MSC units. (c) The MSC pack is completed after adding electrolyte between electrodes [32]. (d) Three-dimensional self-healing MSCs (the original MSCs on the left, sheared MSCs in the middle, and self-healed MSCs on the right) [36]. (e) An image of the transparent MSC device [35]. (f) Photograph of the stretched micro-supercapacitor array when combined with a stretchable substrate. The ruler is 2 cm [16]. (g) Photo of encapsulated and illuminated in combination with micro-LEDs and micro-supercapacitor arrays, stretched by 30% [39]. (h) Time-series photographs of NaCl/Agarose electrolyte samples in phosphate buffered solution (PBS, pH=12, 65°C) [21]. (i) Gelatin-based edible micro-supercapacitors (GEMSCs) housed in a transparent gelatin capsule [45].

3. Integrated systems of micro-supercapacitors

3.1 Integrating with sensors

Micro-supercapacitor with high power density and long cycling life plays a critical role as an in-plane energy storage device. Generally, when the discharging voltage of micro-supercapacitor is higher than or equal to the working voltage of sensors, it can be integrated with energy-consuming sensors, such as photodetectors, gas sensors, temperature sensors and so on, to achieve multifunctional integrated devices.

3.1.1 Integrating with photodetectors

Photodetectors are important components in flexible electronics, and they transform light into electrical signals, playing a vital role in information exchange and environment monitoring. Integrating photodetectors with MSC by wires is a simple way to fabricate an integrated circuit enabling the device with light detecting ability. For instance, Shen [46] displayed an integrated circuits containing a photodetector and MSCs. The photodetector based on CdS nanowires was powered by three tandem rGO-based MSCs and presented a
quick response to the light illumination. Besides, the working voltage of photodetector depended on the number of MSCs, and the signal of responding photo-current of photodetector driven by MSCs was consistent with that of the external power source. Kim [47] built an MSC with multi-walled carbon nanotube (MWNT)/V$_2$O$_5$ nanowire (NW) composites, and combined the MSC with a SnO$_2$ NW UV sensor (Figure 2(a)). The fabricated MSC array could power the UV sensor for 130s, displaying sustainable energy supply. Although the MSCs could provide energy to drive photodetectors for a while, the capacity of symmetric MSCs still needs to be improved to power photodetectors for further application. To this end, Yun [48] employed MnO$_2$ nanoball deposited MWNTs and V$_2$O$_5$ wrapped MWNTs as positive and negative electrodes of asymmetric micro-supercapacitor (AMSC). This AMSC exhibited a high potential up to 1.6V and improved energy density for supplying more energy to photodetectors (Figure 2(b)). Consequently, the photodetector made of ZnO nanowires and patterned graphene could be powered by AMSC for 1500s (Figure 2(c)), indicating a superb energy density of AMSC and well combination between the detector and AMSC. To better integrate AMSC with photodetector, Yang [49] used the free-standing black phosphorus (BP) thin film to both obtain a flexible electrochemical-exfoliated BP nanoflakes based quasi solid-state micro-SCs (QMSC-EE) and a photodetector on one substrate (Figure 2(d)). The photodetector powered by QMSC-EE demonstrates an evident vibration of photocurrent when the light on or off (Figure 2(e)), presenting a stable supplying power of QMSC. To avoid the energy loss of connection joints during integration of MSC and photodetectors, Chen [49] directly coated TiO$_2$ NPs on the buckled SWCNT microelectrodes and combined the UV detector with MSC into one device. The all-in-one system displayed a timely photocurrent response during the process of stretching for 100 times, showing great fitness between UV detector and MSC.

3.1.2 Integrating with gas sensors

Gas sensors are popular elements combined with MSC to monitor the air of environment. The integration techniques of the two parts are similar to the combining way of photodetectors and MSCs. Li [50] reported a MWCNTs/polyaniline (PANI) based
ethanol gas sensor with concentric circular shape, which was powered by electrodeposited polypyrrole (PPy) based MSC arrays for real time detection. The detecting system contained the ethanol gas sensor, MSC array, and printed circuit board (PCB). The resistance of gas sensor would increase when the C₂H₅OH and O₂ reacted to form CO₂ and H₂O. The reaction released electrons to connect with the holes of MWCNT and transformed PANI into emeraldine salt. After the voltage regulator in PCB controlling the MSC voltage to 0.8V, the gas sensor started to monitor the ethanol under a stable electricity served by MSC. The gas sensor was sensitive to multiple concentrations of ethanol ranging from 1 ppm to 200 ppm. In addition, the integrated system also demonstrated good cycling performance under 50 ppm of ethanol concentration, indicating sustainable power supply of MSC and excellent integration of MSC and gas sensor.

Ha [51] introduced a biaxially stretchable NO₂ sensor into MSCs to construct an integrated system on the same stretchable substrate, where NO₂ sensor was fabricated from patterned graphene and MSCs was composed of polyaniline-wrapped MWNTs (PWMWNTs) as the electrodes. The mechanism of NO₂ sensor came from the patterned graphene which absorbed NO₂ to increase its hole concentration and improve its electrical conductivity. The components of the combined device contained twelve PWMWNTs MSCs, gas sensor and gold wire serpentine interconnection on the Ecoflex and SU8 substrate, in which the stretchable substrate enabled the device with stretchability and deformability. When the NO₂ gas at 200 ppm was periodically exposed to gas sensor under the power of MSCs, the current of the sensor increased accordingly. Although the sensitivity and I_{gas}-I_{air} slowly decreased with the number of adsorption/desorption cycles, the curves still presented a good sensitivity to NO₂ gas. Besides, NO₂ gas sensor could be operated normally and steadily powered by MSCs within 50 minutes, presenting a long power-supplying time of MSCs. Apart from that, the stretchable integrated device also displayed stable sensing performance while the uniaxial strain is 50%. Yan [50] further improved the gas sensing system by adding a solar cell for the purpose of charging MnO₂/Ppy based MSCs. The charged MSC then powered a PANI-based NH₃ and HCl gas sensor. In Figure 3(a), a Si-based solar cell charges tandem AMSCs and then the powered MSCs drive the gas sensor to start. It can be observed that the solar cell charges the tandem AMSC for 78 s, which makes the potential of AMSCs reach to a high voltage of 2.82 V. Corresponding charging curve and discharging curve at the current density at 0.1mA cm⁻² are shown in Figure 3(b), where the gas sensor works normally under the tandem AMSCs voltage at 1V and the response current fluctuates with the alternant NH₃ and HCl gas in Figure 3(c), confirming reliable energy output of AMSCs in the integrated system.
Figure 3 (a) Schematic of the tandem AMSC bridging solar cell and gas sensor to store solar energy and supply energy for sensor. (b) Charging curve of the tandem AMSC charged by a commercial solar cell and discharging curve of the tandem AMSC at a current density of 0.1 mA cm\(^{-2}\). (c) Response and recovery curves of PANI-based gas sensor driven by the tandem AMSC when alternately inputting gaseous NH\(_3\) and HCl [52].

### 3.1.3 Integrating with other type of sensors

There are also many other types of sensors constructed with MSCs by adopting MSCs as the power source. For example, Shen [53] built an enzyme-free sweat sensor arrays to examine glucose, [Na\(^+\)] and [K\(^+\)] of human body, and connected the sensor arrays with planar MSCs on a flexible PET substrate. By adding external wireless PCB, a real-time human sweat monitoring system was completed. The cellphone could be wirelessly communicated with the monitor system, clearly showing the values of concentrations of glucose, [Na\(^+\)] and [K\(^+\)]. Besides, curves of the instant current of the sensor indicated that the concentration of glucose, [Na\(^+\)] and [K\(^+\)] were increased with the exercising time going. These results displayed stable energy supply of MSCs to power sensors. Wu [54] developed a self-powered temperature sensing system in Figure 4(a), containing solar cells, temperature sensor and a MXene/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid)-based MSC (MP-MSC). In Figure 4(b), it is demonstrated that the measured current of the temperature sensor increased linearly as the temperature rising. The highest current response value was up to 2.0% at 50°C in Figure 4(c) while utilizing electricity offered by MP-MSC. Conveniently, the MP-MSC could be easily charged by solar cell and provided sustainable long-time repeatable response of 1% during periodical heating cycles (Figure 4(d)). In addition, the integrated sensor system could bear bending angle of 180° and maintain original good response of 95% (Figure 4(e)). It can be concluded that the sensor system enabled with brilliant integration between temperature sensor and MSC, which can be regarded as a wholeness device in wearable electronics. Apart from these, integrated MSCs cooperated with flexible modules are more suitable and applicable for sensing. Han [55] designed a self-powered smart sensor system to test human pulse wave by incorporating all flexible modules on a single piece of PET substrate (Figure 4(f)). Due to the fact that the MSCs and pressure sensor were based on the flexible MXene/BP hybrid film, together with the flexibility of solar cell array, the whole flexible integrated device was fitted closely with the human arm. After being charged for few seconds by solar cells, the MSCs could provide sufficient electricity to the pressure sensor, and the sensor could monitor the changes in the human wrist pulse directly, quickly and precisely.

In general, small and flexible MSCs are easier to integrate with other planar electronics and obtain robust structures. These energy-consuming sensors need sufficient electrical energy of MSCs to work normally, so the size and number of MSCs are required to fit with energy-consuming electronics during integration.
3.2 Integrating with energy-generating device

Although MSC can serve as a power source to energy-consuming electronics, the MSCs also need to be charged by external power equipment, leading to inconvenience for repeated usage of MSCs. In this regard, the integration of MSCs with power generating elements provides an effective solution. Up to now, there are mainly three types of power generating elements integrating with MSCs, including solar cell, piezoelectric energy generator (PEG) or triboelectric nanogenerator (TENG) and wireless charging modules. In theory, all of these energy suppliers should provide high enough voltage to complete fully charge of the corresponding MSCs.

3.2.1 Integrating with solar cell

Solar cell is a commercially available device which generates electricity by absorbing and converting light energy. Many investigators combine solar cell with MSCs to develop an independent self-powered system by wired connection. Mai [56] reported a MSC based on lithium bis(trifluoromethane sulfonyl)imide (LiTFSi) electrolyte by combining with a solar cell as an energy harvester (Figure 5(a)). Owing to the LiTFSi-MSC possessing a high voltage of 2.5 V, the MSC could light a LED after being charged even removing the solar cell off. Likewise, Qu [57] introduced the solar cell into the AMSCs array to drive LED array, in which MnO$_2$@Ppy@MWCNT acted as anode and Ppy@MWCNT as cathode. According to Figure 5(b), the solar cell transformed solar energy into electricity and stored the energy in to a five parallel rows of six series-connected (6S × 5P) AMSCs array, which subsequently powered 2S × 3P LEDs for a long time, showing the AMSC array has good compatibility with solar cell and energy-consuming electronics. Cai [58] delivered a fully equipped solar charging MSC systems that consisting of solar cell, diode, MSC and photodetector, where the diode was to smooth the charging signals by solar cell. The photodetector demonstrated stable current response to UV light, consistent with the current signals of photodetector working under external power source. It can be seen that the solar cell is an efficient module to contribute to a self-powered MSC system. However, this type
of integrated self-powered MSC system not belongs to integrated circuits strictly, because the combined system of MSCs and solar cell is simply constructed by connecting wires with two separated elements, both of which are independent electronics.

Figure 5 (a) Schematic diagram and circuit diagram of integration of a solar cell and carbon-based MSCs activated by ZnO NWs [56]. (b) The integrated self-powered systems using a solar cell as the energy harvester and an AMSC array as the storage unit (SC-AMSCs) [57].

3.2.2 Integrating with PEG or TENG

PEG and TENG are new emerging energy harvesters in electronics, both of which are converting mechanical energy into electricity. PEG is based on the piezoelectric effect caused by mechanical deformation from stress, producing excited charges at the surface of the material, while TENG relies on the coupling effect of contact electrification and electrostatic induction. Integrating PEG or TENG into MSCs is an environmental and convenient way to harvest redundant surrounding mechanical energy.

Zhi [14] connected MSC with PEG as an energy harvesting device in Figure 6(a-b). In the device, PEG harvested the mechanical energy and transformed it into electricity. After rectifying alternating current (AC) into direct current (DC) by rectifier, the electricity was sequentially stored in polypyrrole nanowires based micro-supercapacitor (PPyNW μSC). The charging and discharging curves of μSC in Figure 6(a) (iii) showed that the voltage of MSC achieved to 0.1V by PEG charging for 400s. It is notable that the initial voltage drop is 0.01V, small to be neglected, indicating a perfect integration between MSC and PEG circuits. To examine the stored energy in PPyNW μSC, a red LED was cooperated with it and lit by the releasing electricity, suggesting good integration of PPyNW μSC with electronics. Although the MSC could be charged by the external PEG, the dimensional incompatibility and discrepant stiffness between two components limit their applications on integrated circuits. Zhu [59] successfully integrated two multilayered graphene-MSCs (MG-MSCs) as line-filter, multilayered graphene-polyaniline hybrid MSCs (MG-PANI MSCs), PEG (energy harvester), a diode bridge rectifier (transforming AC into DC), gas sensor and pressure sensor into a flexible PI substrate in Figure 6(c-d). By tapping PEG at 110Hz frequency, the electricity was produced by PEG and stored in MG-PANI MSCs. The charged voltage was up to 1.5 V through rectifier and MG-MSC line-filter (Figure 6(e)).
The current response of the pressure sensor in the integrated device to detect walking pressure pulses (≈5 kPa) is stable in Figure 6(f), where the on/off ratio retains 10000 after 10000 s. After powered by MSCs, pressure sensor detecting multiple steps shows rhythmic signals in Figure 6(g), and PANI gas sensors sensing NO\(_2\) or NH\(_3\) gas under 200 ppm present sensitive and quick response (Figure 6(h)), suggesting that the integrated MSC system worked well in each electrical element.

Jiang [60] assembled TENG with MSC to harvest mechanical energy by contacting and separating the PTFE film and Al electrode under a periodic compressive force at a frequency of 10 Hz generated by oscillator. Rectifier was also used to process AC to DC to charge for MSC (Figure 6(i-j)). In Figure 6(k), eight green LEDs were lit for 1 min under the power provided by three tandem MSCs, which were charged to 3.5 V by TENG. Corresponding charging curves of MSCs displayed fast increasing voltage of MSCs in Figure 6(l), presenting exceptional connections of the integrated system. Conveniently, Dai [61] developed an all-in-one stretchable and wearable self-powered unit, consisting of a single-electrode mode TENG based on carbon-fiber-embedded silicone, a bridge rectifier and a solid-state silicone-encapsulated MXene-based MSC (Figure 6(m-o)). Both of the carbon fiber material and single-electrode mode of TENG alleviated spacer requirements, and enhanced the flexibility and compatibility of the integrated system within a sealed thin silicone film, thus enabling the whole device with deformable and stretchable tolerance. Upon TENG being applied under different frequency (2, 5, and 10 Hz), it is obvious that the MSC charging rate improved with the increase of frequency (Figure 6(p)). The MSC can even be charged to 0.11 V after 200 s under 10 Hz, indicating quick response of MSC to TENG. This all-in-one device exhibited good portability and could be worn directly on human wrist to monitor behavior (Figure 6(m) inset). Subsequently, self-powered ability of the whole device was tested in human motions, including clapping, resting, clapping, resting and clapping corresponding to 5 regions in Figure 6(q). After about 30 minutes, the voltage of the MSC reached to 0.6 V, demonstrating the integrated system has a mechanical energy harvesting ability from human motions. According to the above, the integrated systems composed of MSCs and TENGs (or PEGs) have a trend to be more flexible, light and portable. Furthermore, the integrated system contributed by only one shared substrate shows more compact and robust integration.
Figure 6 (a) (i) The schematic circuit of the mechanical harvesting and storing system by integrating the PEG with PPyNW μSC, (ii) photographs of the PEG-PPyNW integrated system, and (iii) the charging curve of the PPyNW μSC by tapping the PEG and discharging curve. (b) (i) Photographs of an electric device, (ii) PPyNW μSCs connected in series were transferred and attached on the circuit, and (iii) Electric circuit on work powered by PPyNW μSCs [14]. (c) Schematic and electrical circuit diagram of an integrated energy harvesting device. (d) Photograph of the integrated energy harvesting/pressure/gas sensors device. (e) Charging curve of the MG-MSCs by tapping the PEG and discharging curves of MG-MSCs and MG-PANI MSCs at the current of 4 μA cm⁻². (f) Response of current upon the detection of pressure: (g) walking, and (h) exposure to NO₂ and NH₃ [59]. (i) Schematic diagram of the wearable self-charging system, inset photograph demonstrates that the integrated system worn on the forearm. (j) Schematic illustration of mechanism for generating electricity to charge the microsupercapacitor. (k) Circuit diagram of the energy supply mode. (l) Charging curve of the microsupercapacitor charged by TENGs at various frequencies. (m) Charging curve showing the voltage increase of the single capacitor powered by TENG [60]. (n) Schematic diagram of the self-powered nanosystem which is integrated by a triboelectric nanogenerator and three microsupercapacitors (2 cm each). (o) Optical photograph (top) and schematic diagram of the triboelectric nanogenerator (bottom). (p) Optical photograph of 8 commercialized LEDs lighted by charged microsupercapacitors connected in series. (q) Charging curve of three micro-supercapacitors connected in series charged by using the triboelectric nanogenerator [61].

3.2.3 Integrating with wireless charging modules
Electromagnetic energy is an invisible and intangible field energy. Using magnetic field energy for wireless power transmission is a highly efficient charging method. In this case, wireless charging modules are adopted to charge MSCs to obtain integrated devices.

Ha [62] applied a commercial wireless power receiver to charge nine parallel connected array of MSCs with MWCNT as electrodes and poly(ethylene glycol) diacrylate (PEGDA)/1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) as electrolyte. The resultant charged MSCs could power UV/gas sensors (Figure 7(a-b)). The integrated system was fabricated on the Ecoflex substrate and embedded PET films under the whole active devices. In addition, liquid metal Galinstan functioned as interconnections between components. These connections and substrates endowed the system with great tolerance to strain and deformation. After being charged by wireless power receiver, the attached sensors powered by MSCs started to record the biosignals and motion signals. As demonstrated in Figure 7(c-g), the corresponsive signals of repeated body motion, swallowing of saliva and the carotid artery pulse were all successfully detected by the strain sensors under the power of MSCs, showing a credible energy charging of wireless modules and durable energy supply of MSCs in the integrated device. To further increase the integration level of MSCs with wireless charging components, Cai [63] printed a self-made carbon/Ni based wireless charging coil with MSC on one flexible PI substrate (Figure 7(h)). To realize wireless communications with outer, an IC chip was also added into the device to prepare a near-field communication (NFC) tag. It is confirmed that the as-fabricated NFC tag can sensitively communicate with a Blackberry cellphone, and the information of NFC tag could be operated by cellphone interface. This combined system, comprised of wireless charging coil, MSCs and IC chip, provides a new idea to design MSCs into a planar integrated self-powered device. Likewise, Gao [64] added a wireless charging coil to charge for MSCs and released the stored energy in MSCs to drive a photodetector (Figure 7(i-j)). Owing to efficient charging process offered by wireless charging coil, the photodetector operated normally and displayed the current on/off ratios at 1054 (Figure 7(k)), illustrating an excellent connection among charging modules, MSCs and photodetector.

Briefly, most of the wireless powered MSCs of integrated systems are built on a shared substrate to construct an integrated circuit endowed with self-supporting construction. However, the wireless powered MSCs are still in their infancy, because most works simply connect MSCs with wireless charging modules, ignoring mechanical properties and materials compatibility among them, leading to delicate integrated devices.
Figure 7 (a) Photograph of stretchable multisensor system integrated with RF rechargeable energy storage devices. The system consists of a RF power receiver, a MSC array, strain sensor, and UV/NO2 gas sensor. (b) Circuit diagram of integrated system. The schematic diagrams and the properties of the integrated system. (c) Photograph of fragmentized graphene foam sensor attached on neck. (d) Carotid pulse curve obtained before and after exercise. (e) Voice detection curves. (f) Photograph of rock and paper motion using stretchable system attached on wrist. (g) Resistance versus hand motion. (h) A photograph of a real NFC tag integrated with a carbon/Ni composite coil as the NFC antenna for receiving signals and a commercial IC chip for data processing. (i) Circuit diagram of integrated system. The system consists of a coil as power receiver, a MSC, and a photoconductive-type photodetectors of perovskite NWs. (j) Photograph of the integrated system. (k) The photocurrent dependence on time of the device under illumination on/off states driven by the asymmetric MSC.

3.3 All-in-one device

Simply connecting MSCs with other electronics by conductive wires are far from satisfactory in the integrated circuits. All-in-one device is a wholeness system that integrates all components in one intact and compact structure. There are mainly two means of assembling methods at present. One is to bring in multifunctional materials with dynamic reversible properties under special environment, and the other is to design the integrated structure by specific materials with multifunction.

Experiments of dynamic reversible building materials in micro-supercapacitors are rarely investigated, because few types of materials could meet the requirements. Liu [65] reported a stimuli-responsive and photoswitchable MSC based on a diarylethene-graphene composite film with a reversible electrochromic effect. A thin layer of diarylethene derivatives (DAEs) deposited on top of graphene electrodes of MSCs was used as a photoswitchable material. Along with the UV irradiation, the areal capacitance of the assembled MSC increased and gradually saturated after 400s, and the whole capacitance of MSC reached to 120% of its original capacitance. The changeable capacitance was revealed by terahertz (THz) spectroscopy that there was a reversible shift of charge equilibrium at the
DAE/graphene interface while photoisomerization. To verify the restorability of capacitance, the on-off switching of the alternating UV (366 nm, 5 min) and white light (5 min) irradiation was conducted on the MSC, and the MSC presented regular variation upon different irradiations. Apart from a stimuli-responsive electrode material, the electrolyte of MSC is also a dynamic material to change MSC capacitance. In Figure 8(a), Feng [66] prepared a thermoswitchable MSC by utilizing a smart electrolyte, and the electrolyte was obtained from poly(N-isopropylacrylamide)-g-methylcellulose (PNIPAAm/MC) mixing with lithium chloride (LiCl, 0.1M), named as PNIPAAm/MC/LiCl. The side-chain PNIPAAm collapsed during heating and formed a hydrogel through hydrophobic association, hindering the migration of lithium ions among electrodes. Once this copolymer returned to the cooled state, it could be easily stretched back to the relaxed state due to the formation of hydrogen bonds between the N-isopropyl group and water (Figure 8(b)). To demonstrate a thermal dynamic capacitance of MSC, a computer CPU was physically connected with MSCs in Figure 8(c) and Figure 8(f) to form a temperature change window. It is obvious that the capacitance gradually decreases with the increase of temperature (Figure 8(d), (e), (g), (h)), indicating that the thermoswitchable micro-supercapacitor (TS-MSC) has a brilliant cycling performance during repeated heating and cooling procedure. No matter the photoswitchable or the thermoswitchable MSC, the capacitance of MSC can only be changed with special conditions which is still unavailable in most cases, therefore it is demanding that researchers should focus more on those all-in-one MSCs which can change their capacitance according to common variations.

Figure 8 (a) Schematic illustration of the fabrication of a TS-MSC on both a Si wafer and a PI film. (b) Illustration of the reversible sol-gel transition for the thermoresponsive electrolyte and ion transport between interdigital electrodes under heating and cooling. (c) Digital photographs and circuit diagrams of four TS-MSCs connected in series and (f) in parallel on a computer CPU panel under different working conditions. The white-dotted box represents the TS-MSC unit and the other units in the MSC array are the conventional MSCs using PVA/LiCl (C-MSCs). The red and green symbolic capacitors represent the capacitors with switch-on and switch-off states, respectively. Comparison of (d) CV curves at a scan rate of 500 mV s\(^{-1}\) and (e) galvanostatic charge–discharge (GCD) curves at a current density of 40 mA cm\(^{-2}\) for four TS-MSCs connected in series in the 30-80°C temperature range. Comparison of (g) CV curves at a scan rate of 500 mV s\(^{-1}\) and (h) GCD curves at a current
density of 40 mA cm$^{-2}$ for four TS-MSCs connected in parallel in the 30-80°C temperature range [66].

Multifunctional materials are designed in the integrated structure of the all-in-one device. Under the former assembly methods, Zhang [67] cooperated piezoresistance sensor with MSCs to produce an all-in-one sensing patch by using porous carbon nanotube-polydimethylsiloxane (CNT-PDMS) elastomer as both MSC electrodes and sensing part of the piezoresistance sensor. The assembled sensing patch could be attached on the wrists and arms to identify motions according to resistance varying with bending state and compressive strain. Moreover, this sensing patch could be applied as a 3D touch for user identification and safety communication. The touching force and intervals of different persons could be recorded through the sensor, and the user pressed the sensor to login the program by judging their touching habits. Inspired from the 3D structure of the sensing patch, Qu [68] designed an integrated device combining wireless charging coil and MSC into an all-in-one 2D planar chip. A shared electrode (purple line) in Figure 9(a) is proposed to be a part of wireless charging coil and one electrode of MSCs simultaneously. Therefore, the integrated device can not only harvest electromagnetic energy but also store the energy into the MSCs. The as-prepared device is shown in Figure 9(b), where a wireless charging coil is surrounding three parallel MSCs. Besides, the flexibility and robust structure of the seamlessly integrated wireless charging MSCs (IWC-MSCs) is presented in Figure 9(c) by bending the device at a certain angle. During wireless charging test, the induced current of wireless charging coil (WCC) is 2.7 mA and slowly drops (Figure 9(d)) in contrast with the rising induced voltage into WCC which increases from 2.5 V to 4.6 V (Figure 9(e)), indicating that the MSCs is well charged by WCC in the integrated device. Apart from taking a part of building blocks of MSC as a shared component with other electronics, some electronics can be totally act as parts of MSC without any extra constituents to build with MSC. Zhou [67] directly made the separator of supercapacitor (SC) as a power generating equipment. The SC is composed of two carbon nanotube/titanium electrodes, and the separator between electrodes is a membrane made of anodic aluminum oxide (AAO) nanochannels functioning as a power generator with steam (Figure 9(f)). The electrolyte steam could pass through the AAO nanochannels under mechanical pressure and generate streaming potential/current under pressure gradient (Figure 9(g-h)). Operated under 2.5 bar of pressure, the SC stored electric charge density of 0.4 mC cm$^{-2}$ after fully charging by the streaming potential (Figure 9(i)), transforming the mechanical energy into electricity. This all-in-one self-charging electrokinetic supercapacitor provides a totally integrated structure and can be used to harvest and store energy simultaneously.
4. **Challenge and prospect**

In conclusion, we reviewed the recent development of multifunctional MSCs with foldability, stretchability, biocompatibility, and other functions. The integration of MSC with photodetectors, gas sensors and other type of sensors, as well as potential application in energy-consuming electronics was also shown. In addition, self-powered integrated systems of MSCs and energy harvesters including solar cells, PEGs or TENGs, and wireless charging modules, were summarized. All-in-one MSC devices with an intact and compact structure were discussed by designing multifunctional materials into one system. In general, the development of integrated MSC devices from simple, crude connection with metal wires to combination of all components into one shared substrate, and then to an organic unity in all-in-one structure makes the integrated MSCs device become more compact and robust. However, there are still some challenges of micro-supercapacitors integrated systems:

1. Multifunctional MSCs have not been utilized in suitable practical application yet. Most of the investigations only present potentials of the multifunctional MSC applications. For
instance, some stretchable MSCs were reported to bear shape deformations under frequently interactive places and could also replace power source of machines with soft surface. However, few researchers applied them into practical applications, such as acting as a power source for soft and deformable electronic skins. It can be related to the unstable structures and discrepant electrical performances of current multifunctional MSCs under deformation. The deformation may impede their further applications due to these uncertainties. These issues should be focused especially in the process of this field moving towards practicality.

(2) Electrochemical performance of MSCs needs to be enhanced demandingly. During the conjunction with the energy supply power-consuming equipment, such as sensors, it is obviously observed from the detecting curves that the MSCs usually present insufficient energy as a power source displaying gradually weak signals during sensing. This is because MSCs have high power density but a relative low energy density, which are not enough to power energy-consuming electronics for a long time. In this aspect, batteries with high energy density [70-72] can be expected to improve the energy output of microdevices by integrating into the MSCs system. Therefore, rational design and assembly of microbatteries and MSCs as cooperated power source may be helpful for the development of integrated MSCs and sensors devices.

(3) The integration of power management module and MSCs is also required to be improved. Since there is no power-control module while connecting the MSCs with electrical appliance, large quantities of charges will release immediately once connection, resulting in energy waste and a lack of energy in the long-time energy supply. The development of suitable power management modules will help the integrated application of MSCs.

(4) The integrating level of self-powered integrated devices composed of MSCs and energy generators is still far from satisfactory. Loose and rude connectivity between the power generating equipment and MSCs easily causes energy consumption, leading to low charging efficiency and insufficient charging voltage of MSCs. Although the development of structure and integration of MSCs system have solved this problem to a certain extent, few compatible and multifunctional materials can be chosen. Besides, the integrated device structure design is also difficult to meet most practical applications. Therefore, the multifunctional compatible materials and the structural design of integrated devices between MSCs and other electronic components should be developed in future MSC integrated devices.

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