ORIGINAL RESEARCH ARTICLE

In-Plane Flexible Microsystems Integrated with High-Performance Microsupercapacitors and Photodetectors

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The rapid development of wearable and portable electronics has resulted in an urgent desire for lightweight, flexible microsystems integrated with energy storage devices and other in-plane devices. An approach is proposed herein to develop an in-plane flexible microsystem on graphite paper containing an all-solid-state microsupercapacitor and a photoconductor-type photodetector based on perovskite film, where a simple, low-cost, and scalable strategy involving laser etching, electrochemical exfoliation, and electrochemical deposition can be used to fabricate the all-solid-state microsupercapacitor. The as-fabricated microsupercapacitor device exhibits high capacitance and reliable stability under testing through 100,000 cycles of dynamic bending. In the integrated microsystem, the microsupercapacitor is used to drive the photoconductive detector. It turns out that the designed integrated system exhibits a stable photocurrent response comparable to a detector driven by an external power source. This work paves the way for the fabrication of integrated microsystems where sensor systems are driven by integrated energy storage devices, applicable to future wearable and portable electronics.

Key words: Microsupercapacitor, all-solid-state, in-plane, flexible, integrated microsystems

INTRODUCTION

With the current rapid development of wearable and portable electronics, more attention is being paid to flexible integrated microsystems.¹ To satisfy the requirements of specific wearable and portable applications, such integrated systems require a combination of energy storage and operational units integrated into a flexible plane, which can enable systems with smaller volumes and avoid complex connections between the units.^{2–4}

In such a flexible system, the energy storage unit plays a crucial role in the operation of the overall system. Microsupercapacitors (MSCs), with two-dimensional interdigitated patterns as the conductive path, are preferred for on-chip electronics because they can charge/discharge in a short time and are easier to integrate with other in-plane devices to build up the whole flexible system.^{5–8} Much research into integrated systems containing MSCs and other sensing devices has been reported; For example, Yun et al. fabricated an integrated system where a gas sensor based on stretchable patterned graphene was driven by an MSC array.⁹ Chen et al. reported a strategy to prepare a highly stretchable integrated system based on an MSC and

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ultraviolet (UV) detector.¹⁰ Yue et al. proposed a scalable strategy to fabricate a flexible integrated system on a plane substrate containing an MSC, photodetector, and wireless charging coil.¹¹ Such integrated systems driven by MSCs can operate well to meet the requirements of wearable and portable electronics applications. However, to achieve scalable production of wearable and portable integrated systems, more research must be carried out.

An important area for such integrated microsystems is the search for low-cost, simple, and scalable methods to fabricate the patterned in-plane microelectrodes that serve as conductive collectors for both MSCs and the operational units. Such in-plane microelectrodes are typically fabricated using the photolithography technique, then a thin film is deposited on the substrate by e-beam evaporation^{12,13} or magnetron sputtering^{14,15} to form the patterned microelectrodes. Although such patterned collectors are highly conductive, the resulting film with low surface area limits the performance of the individual units such as the MSCs. In contrast to this high-cost, complex process and time-consuming method, many new methods have been proposed to manufacture microelectrodes for integrated microsystems.^{16–19} For instance, Gao et al. reported a direct laser writing method to fabricate reduced graphene oxide microelectrodes by laser-induced reduction of graphene oxide.²⁰ Lin et al. fabricated three-dimensional (3D) porous graphene microelectrodes from a polymer substrate using a laser-induced method.²¹ Yue et al. used ink printing and electrochemical deposition to fabricate MSC microelectrodes.¹¹ Such simple, low-cost strategies for fabricating flexible microelectrodes for MSC devices and operational units are needed to achieve scalable production of wearable and portable integrated microsystems.

To make the whole integrated system work reliably requires MSC devices and operational units with high performance. The low specific capacitance of MSCs hinders their practical development in various fields.²² There remains an urgent desire to fabricate MSCs with high performance. More research attention is thus being paid to the integration of pseudo-material onto the collector to improve the capacitance of such device, such as manganese dioxide (MnO_2),¹¹ vanadium oxides,²³ polyaniline (PANI),²⁴ and polypyrrole (PPy).²⁵ However, due to the low surface area resulting from the smooth substrate and the poor conductivity of the active material, a limited increase in capacitance and poor rate capability are obtained. Another effective strategy is to fabricate collectors with high surface area. Carbon nanotubes (CNTs),^{26,27} CNT/reduced graphene oxide,²⁸ and graphene^{29–31} have been employed to improve the specific surface area of the substrate. However, these methods are high cost, and their fabrication processes are complex. It is thus necessary to fabricate high-surface-area

collectors to obtain MSC devices with high performance.

An approach is proposed herein to develop an in-plane flexible integrated microsystem based on graphite paper, where an all-solid-state microsupercapacitor is used to drive a photoconductor-type photodetector based on perovskite film. The flexible MSC devices are fabricated using a simple, low-cost, and scalable strategy that involves laser etching, electrochemical exfoliation, and electrochemical deposition. The MSC device exhibits high capacitance and reliable stability through a 10^5 -cycle bending test, which can be attributed to the enhanced surface area of the collector resulting from the electrochemical exfoliation process, the pseudocapacitance originating from the electrodeposited MnO_2 , and the good adhesion achieved between the active material and the rough collector. Furthermore, the integrated system exhibits a stable photocurrent response comparable to a detector driven by an external power source, demonstrating the feasibility of such integrated flexible systems. This strategy provides a route for the simple and scalable fabrication of wearable and portable integrated electronic devices.

EXPERIMENTAL PROCEDURES

Synthesis and Fabrication of Carbon Paper Interdigitated Electrodes

Graphite paper was purchased from Hente Company, Hebei. A CO_2 laser cutter system (Universal X-660) was used to etch the graphite paper at a power of 4.8 W. Graphite paper (CP) was patterned into ten interdigitated electrodes with length of ~ 10 mm, width of ~ 620 μm , and spacing of ~ 200 μm between two neighboring microelectrodes (Supplementary Fig. S7). The patterned CP was carefully dry-transferred to polyethylene terephthalate (PET) using double-sided tape (3M Company, 9080) to avoid contact between neighboring microelectrodes. All samples were prepared at room temperature under ambient air.

Electrochemical Exfoliation of CP

Electrochemical exfoliation of the CP was carried out in a two-electrode system. CP on PET sheet served as the working electrode, which was immersed into aqueous solution containing 0.5 M KNO_3 at room temperature. Platinum foil (Sigma-Aldrich) was used as the counterelectrode. Exfoliation was conducted at constant potential of 8 V for 30 s, then changed to the other side to apply the same exfoliation. The exfoliated carbon paper is denoted as ECP. Finally, the as-prepared electrode was washed with deionized water and ethanol to remove any impurities.

Electrodeposition of MnO_2 on ECP

Electrodeposition was carried out using a three-electrode setup with ECP as the working electrode, and platinum foil (Sigma-Aldrich) and Ag/AgCl (Fisher Scientific) as counter and reference electrode, respectively. MnO_2 was deposited on ECP using cyclic voltammetry from 0.4 V to 1.3 V versus Ag/AgCl at 20 mV s^{-1} for four cycles in an aqueous mixture of 20 mM manganese nitrate and 100 mM sodium nitrate at ambient conditions. The other side was then subjected to electrochemical deposition for another four cycles. After deposition, the sample was withdrawn and washed with deionized (DI) water to remove excess electrolyte, then placed in a vacuum drier overnight. The obtained sample is denoted as ECP-8 MnO_2 . The mass loading of MnO_2 deposited on the ECP- MnO_2 electrode was about 0.21 mg/cm^2 . For comparison, ECP-6 MnO_2 and ECP-10 MnO_2 were obtained by electrodeposition for three and five cycles on each side, respectively.

Electrodeposition of MnO_2 on CP

For comparison, CP-8 MnO_2 samples were obtained by electrodeposition for four cycles for each side of the CP electrode using the similar method except for the different working electrode.

Fabrication of Flexible All-Solid-State Symmetric MSCs

Polymeric gel electrolytes formed of polyvinyl alcohol (PVA)/lithium chloride (LiCl) were prepared as described previously.^{32,33} PVA/LiCl was fabricated by stirring 10 mL DI water, 2.0 g LiCl (Sigma-Aldrich), and 1.0 g PVA ($M_w = 50,000 \text{ g mol}^{-1}$, Aldrich No. 34158-4) at 80°C overnight. The active area of the MSCs was coated by the electrolyte and dried at ambient conditions for 4 h. Finally, MSCs were obtained after drying in vacuum desiccators overnight for further solidification of the electrolyte.

Fabrication of Patterned Liquid Metal Interconnections

Galinstan (Gallium Source Company) consisting of gallium (68.5%), indium (21.5%), and tin (10%) has excellent conductivity and was chosen to serve as the liquid metal interconnections to integrate the fabricated MSCs and photodetector. Here, Scotch Magic Tape (3M Company), which shows affinity to Galinstan, was used to draw guide lines to pattern the liquid metal Galinstan. Tape with a line width of $700 \mu\text{m}$ was attached to the PET substrate to serve as the liquid metal channel, then holes with diameter of 2 mm were punched to connect the devices on the upper side and the liquid metal channel on the other side of the PET substrate. The liquid metal pattern was fabricated along the channel on the tape by injecting Galinstan using a syringe. Finally, the patterned liquid metal line was encapsulated with spin-coated polydimethylsiloxane (PDMS) at

400 rpm for 45 s and heated at 80°C for 5 min to obtain the final samples.

Integration of MSCs and Photodetector

To integrate the MSCs and photodetector on the PET substrate, a dry transfer method with double-sided adhesive tape (3M Company) was used. The double-sided adhesive tape were attached to the bottom side of the MSC and photodetector device. After punching holes with diameter of 2 mm, the devices were attached to the PET substrate by patterned liquid metal interconnections. Ag paste (Elcoat) was deposited onto the contacts between the device electrodes and patterned interconnections and cured at room temperature, resulting in integrated devices with good interconnection.

Fabrication of Perovskite-Based Photodetector

Lead iodide (PbI_2 , 517 mg), formamidinium iodine (FAI, 171 mg), methylamine bromide (MABr, 23.2 mg), lead bromide (PbBr_2 , 73.4 mg) were dispersed in 0.75 mL dimethylformamide (DMF) and 0.25 mL dimethyl sulfoxide (DMSO) to form perovskite precursor solution, then 390 mg/mL cesium iodide (CsI) solution in DMSO was added to the precursor solution, followed by stirring for more than 2 h. The solution was dropped onto the graphite paper with interdigitated electrodes, followed by spinning at 500 rpm for 30 s. Finally, the perovskite-based photodetector was obtained after drying at 100°C for 1 h.

Characterization and Electrochemical Measurements

The morphology of the CP, ECP, and ECP- MnO_2 nanostructures was studied by field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL). Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were conducted on the MSC devices using an Autolab workstation (PGSTAT-302N) and battery measurement system (LAND-CT2001A), respectively. The cycling performance of the devices was also tested using a LAND-CT2001A. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a PGSTAT-302N by applying an alternating-current (AC) voltage with amplitude of 5 mV in the frequency range from 100 kHz to 0.01 Hz at open-circuit potential. To test the fatigue resistance of the MSCs, polyimide (PI) tape was encapsulated on the active area of the MSC device to prevent the gel electrolyte from adhering to the machine. Dynamic testing was conducted using a bending machine set at a frequency of 5 Hz.

Calculation of Area Capacitance, Energy, and Power Density

The areal specific capacitance (C_A) of the electrode materials was calculated from the galvanostatic charge–discharge curves using Eq. 1:

$$C_A = 4I / (A_{\text{device}} \times (dV/dt)), \quad (1)$$

where I is the applied current, A_{device} is the total active area of the device, and dV/dt is the slope of the discharge curve.

The areal capacitance (C_{device}) was calculated by using Eq. 2:

$$C_{\text{device}} = C_A / 4. \quad (2)$$

The areal energy density (E_{device}) and power density (P_{device}) of the MSCs were calculated by using Eq. 3 and 4, respectively:

$$E_{\text{device}} = C_{\text{device}} \times V^2 / (2 \times 3600), \quad (3)$$

$$P = E_{\text{device}} \times 3600 / \Delta t, \quad (4)$$

where V is the applied voltage and Δt is the discharge time.

RESULTS AND DISCUSSION

The fabrication process for the flexible MSC devices is shown in Fig. 1a. Firstly, laser etching is carried out on the carbon paper substrate to form the patterned CP with ten in-plane interdigitated electrodes (five per polarity). Then, electrochemical exfoliation is conducted to obtain the high-surface-area collector ECP. The pseudocapacitive material MnO_2 is electrodeposited on the ECP to form the ECP- MnO_2 composite. The amount of active material in the composites can be easily controlled by adjusting the deposition cycles, here being labeled as ECP- $X\text{MnO}_2$ (where X is the total number of deposition cycles). Details on the ECP synthesis and electrodeposition of MnO_2 can be found in “Experimental Procedures” section. Solid-state polymer electrolyte containing PVA and LiCl is dropped on the ECP- $X\text{MnO}_2$ to complete the fabrication of the MSC devices. Figure 1h shows a digital photograph of one fully fabricated MSC device obtained using this method. The CP consists of ten pairs of finger electrodes. The finger length is ~ 10 mm, the average finger width is ~ 620 μm , and the average gap between fingers is ~ 200 μm (as shown in the optical image in Fig. 1i). It must be pointed out that the width of the gap is not fixed due to the dry transfer method applied here. Figure 1b shows scanning electron microscopy (SEM) images of CP. Two gaps and interdigitated fingers are observed on the PET film, which is fixed with double-sided tape. A high-magnification SEM image of CP is shown in Fig. 1e, revealing a smooth surface. After electrochemical exfoliation, a rather rough surface is

observed, with large graphite lamellae distributed on it (Fig. 1c). A high-magnification SEM image of ECP is presented in Fig. 1f, where a rough and crumpled graphite layer is seen. The rough structure obtained after electrochemical exfoliation exhibits a higher surface area, which can serve as a conductive matrix for the subsequent deposition of MnO_2 . The number of deposition cycles can be varied to control the average mass of MnO_2 on the collector. An SEM image of ECP- 8MnO_2 is shown in Fig. 1d, g, revealing a thick film on the graphite paper. The higher-magnification SEM image in Fig. 1j further verifies the nanostructure of the deposited MnO_2 , where MnO_2 with flower-like shape is interconnected and covers the ECP surface. These results suggest that these samples with high surface area have great potential for further electrochemical testing. Cross-section SEM images in the as-prepared state are also shown in Supplementary Fig. S1. A smooth cross-section is observed for the CP samples, whereas it becomes very rough with some graphite sheet distributed on the surface of the ECP samples. After electrochemical deposition, the ECP- MnO_2 samples show a rougher structure. To investigate the effect of the mass loading of MnO_2 on the morphology, the nanostructure after different numbers of electrochemical deposition cycles of MnO_2 is shown by SEM in Supplementary Fig. S2. Thin clusters are distributed on the surface of the ECP- 6MnO_2 . As the number of electrochemical deposition cycles is increased, the clusters interlock and become interconnected, thereby covering the whole surface. However, as the number of deposition cycles is increased, the ECP- 10MnO_2 samples show thick clusters, indicating that the nanostructures gather together at the cost of a certain amount of surface area. Therefore, ECP- 8MnO_2 with the high-surface-area nanostructure is optimal for further testing. x-ray photoelectron spectroscopy was also carried out to study the composition of the composites (Supplementary Fig. S3), further confirming the presence of MnO_2 in the composite.^{34,35}

To demonstrate the electrochemical performance of the as-prepared MSCs with LiCl/PVA as electrolyte, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) experiments were carried out in the potential window from 0 V to 0.8 V. Figure 2a shows the CV curves obtained for CP, ECP, CP- 8MnO_2 , and ECP- 8MnO_2 MSCs at a scan rate of 50 mV s^{-1} . After electrochemical exfoliation, the capacitance of the MSCs increased greatly. MnO_2 is deposited on the CP and ECP to obtain the CP- MnO_2 and ECP- MnO_2 MSCs. Obviously, the ECP- MnO_2 MSCs displayed a wider CV window than CP- MnO_2 . GCD measurements at the same current density were also conducted to verify these results. As shown in Fig. 2b, the ECP- MnO_2 MSC exhibited a longer discharge time than the CP- MnO_2 and ECP MSCs, indicating higher capacitance. The capacitance calculated from the GCD curves is shown in Fig. 2c. The ECP- MnO_2 MSC

Fig. 1. Fabrication of MSCs. Schematic diagram of fabrication process of MSC on PET (a). Low- and high-magnitude SEM images of finger electrode of CP (b, e), ECP (c, f), and ECP-MnO₂ (d, g). Digital image of interdigitated fingers of ECP-8MnO₂ (h). Optical image of selected several fingers of CP (i). Enlarged high-magnitude SEM images of ECP-MnO₂ (j).

Fig. 2. Electrochemical performance of MSCs. (a) CV profiles obtained at scan rate of 50 mV s^{-1} . (b) GCD curves of different MSCs at current density of 0.2 mA cm^{-2} . (c) Areal capacitance derived from GCD curves in (b). (d) CV profiles of MSCs obtained using different numbers of deposition cycles. (e) CV profiles of ECP-8MnO₂ at different scan rates. (f) GCD curves of ECP-8MnO₂ at different discharge current densities. (g) Areal capacitance derived from GCD curves in (f). (h) Nyquist plot collected at open-circuit potential from 100 kHz to 0.01 Hz with perturbation of 5 mV. (i) Cycle performance of MSC at current density of 0.8 mA .

exhibited a capacitance of 82.9 mF cm^{-2} , while the value was 7.0 and 12.4 mF cm^{-2} for the CP-MnO₂ and ECP MSCs, respectively. These results illustrate that electrochemical exfoliation is beneficial to obtain a high-surface-area carbon matrix to serve as the substrate, and that electrochemical deposition of the pseudomaterial MnO₂ significantly increased the capacitance of the whole composite. Benefiting from the synergistic effect of these two points, the ECP-MnO₂ MSCs showed outstanding capacitance. To further explore the effect of the mass of MnO₂ on the performance of MSCs, CV testing of ECP-MnO₂ MSCs obtained using different numbers of deposition cycles was performed; the results are shown in Fig. 2d. When the number of deposition cycles was increased from six to eight, the CV window of ECP-MnO₂ became wider. The voltage window got narrower when the number of deposition cycles was further increased, which may be related to the nanostructure obtained after different numbers of electrochemical deposition cycles of MnO₂ in

Supplementary Fig. S2. As the number of deposition cycles was increased further, the gathered MnO₂ structure led to a decrease in the surface area and poor conductivity, thus causing fading of the capacitance and poor rate capability, manifested as a narrower voltage window. Therefore, MnO₂ deposition for eight cycles was optimal to obtain an MSC with the highest capacitance. The CV profiles of ECP-8MnO₂ MSCs obtained at different scan rates are shown in Fig. 2e. At lower scan rates, the MSC exhibited a nearly rectangular shape, indicating pure supercapacitive behavior with small equivalent series resistance (ESR). As the scan rate was increased, the CV curves became distorted. This indicates that the MSC became more resistive, caused by an increase in IR effects.^{36,37} The GCD curves of the ECP-MnO₂ samples obtained using different numbers of deposition cycles are shown in Fig. 2f and Supplementary Fig. S4. At a current density of 0.1 mA , the charge time was obviously longer than the discharge time for the ECP-8MnO₂

MSC device. The GCD curves of ECP-6MnO₂ and ECP-10MnO₂ at different discharge current densities are shown in Supplementary Fig. S5. The GCD curves of ECP-8MnO₂ at higher current densities from 0.8 mA to 2 mA are shown in Supplementary Fig. S6. As the current density was increased, the GCD curves became more linear and symmetrical, indicating good reversibility.³⁸ The capacitance calculated from the GCD curves is shown in Fig. 2g and Supplementary Fig. S6b. ECP-8MnO₂ exhibited a high capacitance of 101.4 mF cm⁻² at a current density of 0.1 mA. Even when the current density was increased to 0.8 mA, a capacitance of 68.9 mF cm⁻² was still retained. ECP-10MnO₂ and ECP-6MnO₂ showed specific capacitance values around 20 mF cm⁻² to 40 mF cm⁻². The decrease in the capacitance with increasing mass loading of MnO₂ is mainly caused by the gathering of the nanostructure, which leads to a decreased surface area and fading capacitance.

Electrochemical impedance spectroscopy (EIS) was also conducted to further study the electrochemical behavior of the ECP-8MnO₂ MSC device. As shown in Fig. 2h, the Nyquist plot was composed of a small arc at high frequency and a straight line at low frequency. The shallow slope observed in the low-frequency domain indicates limited ion transport in the gel electrolyte.^{33,39} The equivalent series resistance obtained from the intercept of the plot with the real axis is only 20 Ω cm⁻², which can be attributed to the conductivity of the composites. Long cycling life is another important requirement for supercapacitors. The cycle life of the ECP-8MnO₂ MSC device was tested in the potential window from 0 V to 0.8 V at a current of 0.8 mA for 2000 cycles (Fig. 2i). After 2000 cycles, the capacitance of the ECP-8MnO₂ MSC device remained above 94.2% of its value in the first cycle, corresponding to a coulombic efficiency of more than 95.7%. This demonstrates the good cycling performance of the MSC device.

To meet the requirements of various practical applications, supercapacitors are usually connected in parallel and series to achieve the required capacitance and voltage.^{40,41} As shown in Fig. 3a, placing two MSCs in parallel resulted in approximately twice the current of a single device when charging/discharging at the same current density, yielding twofold higher capacitance in comparison with a single MSC. Connecting two MSCs in series could extend the voltage window up to 1.6 V while maintaining the same charging/discharging time, indicating that half of the capacitance is sacrificed in comparison with a single device (Fig. 3b). To verify the practical application of the MSCs, four single MSCs were assembled in series on a PET film, connected by liquid metal. Red light-emitting diodes (LEDs, 3 V, 10 mA to 20 mA) as well as a switch were also adhered to the PET. It was found that the red LED could be lit when the switch was turned on (Fig. 3c). Eight blue LEDs (2.4 V, 10 mA

to 20 mA) in parallel could also be lit by the four MSCs in series. Figure 3d shows a schematic diagram of an LCD (1.5 V) driven by four MSCs connected in series. As shown in the digital photograph in Fig. 3e, the LCD driven by the MSCs could operate for more than 40 min. These results suggest that such MSC devices have great potential for use in practical applications, such as flexible electronics device requiring long-duration energy supply.

The flexibility of an in-plane MSC is essential for practical applications, especially when integrated into flexible and wearable electronics.^{10,42} Static and dynamic testing of a single MSC device was therefore carried out in the bending state. Digital photographs of one MSC at different angles are shown in Fig. 3g. The static CV plots of the device in different bending states are shown in Fig. 3f. No obvious changes in the CV area are observed for the MSC device under different bending states. Dynamic testing was conducted using a bending machine set at a frequency of 5 Hz. Before testing, a polyimide (PI) tape was encapsulated on the active area of the MSC device to prevent the gel electrolyte from adhering to the machine. As shown in Fig. 3h, the dynamic cycling testing did not result in an obvious degradation of the CV area. The capacitance retention over 10⁵ cycles of dynamic testing (at a bending radius of 3 mm) is shown in Fig. 3i. After 10⁵ cycles, 92% of the capacitance of the first cycle was retained. In particular, a capacitance increase can be observed after 25,000 bending cycles, which can mainly be attributed to the fact that more ions from the gel electrolyte become available at the interface between the electrode and electrolyte with increased bending cycles. This superior fatigue resistance can be attributed to the strong interfacial adhesion and encapsulation by the PI tape. In particular: (1) The laser-etched graphite paper is dry-transferred onto the PET using double-side taped, resulting in improved interfacial adhesion between the graphite paper and PET substrate. (2) The porous and rough structure of the electrochemical exfoliated graphite paper enhances the interfacial adhesion between the MnO₂ and graphite paper. (3) The encapsulation by the PI tape retains the humidity of the gel electrolyte, thereby preventing severe degradation of the electrochemical performance. These results illustrate that the as-fabricated MSC could endure harsh mechanical deformations, such as dynamic bending.

The energy density and power density are important parameters to evaluate the performance of supercapacitors. As shown in Fig. 4, a maximum energy density of 8.82 μW h cm⁻² was obtained at a power density of 0.095 mW cm⁻², while the maximum power density was 0.715 mW cm⁻² at an energy density of 14.64 mW h cm⁻². These energy densities achieved with the MnO₂ symmetric MSCs based on exfoliated graphite paper are comparable to values reported for other MSCs, such as MnO₂/Ni

Fig. 3. GCD curves for two ECP-8MnO₂ MSC devices connected in parallel (a) or series (b). One (left) and eight (right) LEDs powered by four MSC devices in series (c). Schematic diagram (d) and digital image (e) of electronic watch powered by four MSC devices in series. CV plots (f) and digital photograph (g) of MSC at different bending angles. (h) CV profiles of the 1st, 10⁴th, 5 × 10⁴th, and 10⁵th cycles. (i) Cycling performance of MSC at bending radius of 2 mm; inset shows a digital photograph of an MSC in bent state.

Fig. 4. Ragone plot of MnO₂ symmetric MSCs based on exfoliated graphite paper compared with other energy storage devices.

symmetric,⁴² Au/MnO₂/Au multilayer,¹⁴ MnO₂/multilayered carbon nanotube (MWCNT)/V₂O₅/

MWCNT asymmetric,⁴³ hybrid MWCNT/PANI,⁴⁴ reduced graphene oxide symmetric,⁴⁵ MXene (Y-Ti₃C₂T_x),⁴⁶ and MXene film double-sided⁴⁷ structures.

To determine the feasibility of using such as-prepared MSC devices in wearable and flexible electronics, the fabricated MSC devices were integrated with a photodetector on one piece of PET film. As shown schematically in Fig. 5a, the photodetector was connected to the MSC device with an ammeter in series connection with them. Perovskite serves as the photosensitive material for the photodetection due to its high photoresponse.^{48,49} A photodetection experiment was performed at room temperature in ambient air condition. During the photodetection, a solar light simulator was repeated turned on or off without any extra control of the external conditions such as the changes in temperature or atmosphere.^{50,51} Figure 5b shows optical and digital images of the photodetector, where a dark-blue perovskite film is observed. The SEM image shown in Fig. 5c exhibits a

Fig. 5. Integration of one MSC and photodetector on one piece of PET film. (a) Schematic of related electric circuit. (b) Optical graph of photodetector based on perovskite film; Inset shows digital image of photodetector. (c) SEM image of perovskite film. (d) Self-discharge curve of one MSC device. Photocurrent versus time plots of photodetector under illumination at bias of 0.48 V driven by the external conventional power source (e) or supplied by the MSC device (f).

compact, homogeneous, and smooth perovskite film. The self-discharge performance of the MSC device was studied. As shown in Fig. 5d, one MSC device could keep the potential above 0.48 V for over 7000 s after being fully charged, indicating the possibility of driving devices for a long time. To validate the photodetection properties of the device, the photoconductive-type detector was measured under white illumination and in the dark. Figure 5e shows the photoresponse of the photodetector when powered by an external source. The obvious difference in the photocurrent between the white illumination and in the dark indicates the potential of such perovskite-based photodetectors for practical applications. When the illumination was switched alternately on and off, the photocurrent of the device was stimulated and shut down in turn. At a bias voltage of 0.48 V, the on/off current ratio of the photodetector was around 95, indicating the outstanding performance of the perovskite-based photodetector. The as-prepared MSC device was also used to drive the photodetector. As shown in Fig. 4f, the photo-sensing current and on/off ratio current were comparable to when the photodetector was supplied by the external source. This illustrates the feasibility of using such MSCs to provide the power required to drive photoconductive-type detectors. It is also suggested that the MSC has great potential as a flexible energy storage device for integration with flexible and wearable electronics.

CONCLUSIONS

An approach is proposed to develop an in-plane flexible microsystem integrating an all-solid-state flexible MSC device and a photoconductive-type photodetector based on perovskite film. The MSC device was fabricated using a simple and scalable strategy, which involves laser etching, electrochemical exfoliation, and electrochemical deposition. Benefiting from the electrochemical exfoliation method, an enhanced surface area was obtained for the collector. Based on the advantages of this enhanced surface area, the large pseudocapacitance of the MnO_2 , and the enhanced adhesion between the active material and collector, the as-fabricated MSC device showed outstanding performance, including high capacitance and reliable stability during long-cycle bending testing. Furthermore, the designed integrated system, where MSC devices are used to drive the photoconductive detector, exhibits a stable photocurrent response comparable to the detector driven by an external power source, thus demonstrating the feasibility of constructing a flexible integrated system on one chip. This study provides useful insights into improving the performance of microsupercapacitors by exfoliating collectors and an important routine to fabricate integrated systems for portable and wearable electronics.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

SUPPLEMENTARY INFORMATION

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