High-Voltage Flexible Microsupercapacitors Based on Laser-Induced Graphene

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ABSTRACT: High-voltage energy-storage devices are quite commonly needed for robots and dielectric elastomers. This paper presents a flexible high-voltage microsupercapacitor (MSC) with a planar in-series architecture for the first time based on laser-induced graphene. The high-voltage devices are capable of supplying output voltages ranging from a few to thousands of volts. The measured capacitances for the 1, 3, and 6 V MSCs were 60.5, 20.7, and 10.0 μF, respectively, under an applied current of 1.0 μA. After the 5000-cycle charge–discharge test, the 6 V MSC retained about 97.8% of the initial capacitance. It also was recorded that the all-solid-state 209 V MSC could achieve a high capacitance of 0.43 μF at a low applied current of 0.2 μA and a capacitance of 0.18 μF even at a high applied current of 5.0 μA. We further demonstrate the robust function of our flexible high-voltage MSCs by using them to power a piezoresistive microsensor (6 V) and a walking robot (>2000 V). Considering the simple, direct, and cost-effective fabrication method of our laser-fabricated flexible high-voltage MSCs, this work paves the way and lays the foundation for high-voltage energy-storage devices.

KEYWORDS: high voltage, laser-induced graphene, microsupercapacitors, microsensors, microrobots

INTRODUCTION

High-voltage power supplies are quite commonly required for many electronics and machines like small robots,4–5 and dielectric elastomers.4–6 To obtain high-voltage output, batteries and supercapacitors are usually connected in series by cables because they could only offer less than 4 V for a single cell. But such connection always suffers from inconvenience of operation by using plenty of conducting metal wires.

Supercapacitors have been viewed as a valuable alternative to batteries because they can be charged and discharged much more rapidly with an almost infinite lifetime.15 Unlike batteries that rely on electrochemical redox reactions, a supercapacitor stores charges via the adsorption and desorption of ions within a thin electrical double layer that exists between the solid electrodes and the bulk electrolytes.14,15 This allows adsorbed ions to rapidly desorb from the surface of the electrodes, enabling a supercapacitor to attain high power density by discharging and releasing power within a short time. Miniaturized supercapacitors, commonly known as microsupercapacitors (MSCs), have become an active and intense area of research.16–18 This phenomenon is catalyzed by the popularity and rise of miniaturized, self-powering electronics, which necessitates direct integration of miniaturized, on-chip energy-storage devices, such as supercapacitors, on a flexible platform.19–21 Increasingly, these micro energy-storage devices are designed to power microelectronics, such as wireless microsensors networks22,23 and radio-frequency identification tags.24,25 Some of the microelectronics are driven by high-voltage sources from a few to thousands of volts. Nevertheless, the intrinsic low output voltage (typically less than 4 V) of MSCs, critically limited by the properties of electrode materials and electrolyte, presents a formidable challenge and obstacle in their use in directly powering such microelectronics. To this end, a workable strategy to make high-voltage MSCs is to assemble many MSCs into a high-voltage energy stack via in-series connection using external conducting metal wires. The resulting assemblies, however, suffer from critical drawbacks in operation safety and complex fabrication processes.26 Therefore, a safe, simple, and effective means to directly integrate high-voltage MSCs with microelectronics, albeit difficult and elusive at present, remains important and desirable.
Herein, by using the in-series structure, flexible high-voltage planar MSCs based on laser-induced graphene (LIG) can generate an output voltage of up to 209 V for the first time, which was the highest recorded voltage among all current planar MSCs. In other words, 210 LIG square electrodes were fabricated via a direct-write, ambient laser pyrolysis of polyimide film first and then 209 single-unit microsupercapacitors were connected in series on a single-film substrate. Compared to the lithographic processes that may involve multiple masking steps, direct laser writing provides a fast and low-cost fabrication route that enables substantially faster design iterations. Furthermore, to investigate the electrochemical performance of high-voltage MSCs, cyclic voltammetry (CV) and charge−discharge methods at high-voltage range (0−209 V) were developed in this work. Besides, we successfully applied the highly robust MSC in powering piezoresistive microsensors in the application of a walking step counter (pedometer) for activity tracking. Besides, ten 209 V MSCs were also connected in series to drive small walking robots, which need the 2000 V power source.

■ RESULTS AND DISCUSSION

The laser-assisted fabrication and electrolyte coating processes are schematically shown in Figure 1a. Briefly, the 209 V MSC patterns were designed by using a pattern-generation software and transferred to a programmable CO2 infrared laser system. Next, a 125 μm thick Kapton (polyimide) substrate was rapidly and irreversibly pyrolyzed by a laser beam (wavelength, 10.6 μm; laser spot size, 200 μm) with an optimized scan rate of 250 mm/s and a power of 8.0 W. Upon the transient laser heating, the surface of the Kapton substrate was instantaneously transformed into a porous graphene network, which exhibited good physical and electrical characteristics suitable for potential energy-storage applications. To construct a 209 V
MSC, 210 porous LIG squares (3 mm × 3 mm for each square) separated by 209 gaps (500 μm in distance) were laser-patterned (inset on the left of Figure 1a). Moreover, each gap and an estimated 30% area from one side of the LIG square, approximated from Figure S1, were covered with 1.0 M H2SO4−poly(vinyl alcohol) (PVA) electrolyte. The middle section of each LIG square can act as the common conductive electrode for the in-series connections without the coating of the H2SO4−PVA electrolyte. The shear viscosity of H2SO4−PVA was as high as 5738 Pa s at room temperature (Figure S2), and a droplet-shape electrolyte was plotted at the gap using a tiny brush (PRINCETON Lauren 4035R, Figure S3).

The transient laser heating temperature (at 0.1 ms) on the Kapton film (125 μm in thickness) was simulated by COMSOL Multiphysics to be about 1609.8°C when the laser power output and scan speed were set at 8.0 W and 250 mm/s, respectively, as shown in Figure 1b. Figure 1c illustrates that as the laser power increased from 4.0 to 8.0 W, the simulated temperature increased from 817.2 to 1609.8°C, whereas the sheet resistance of the LIG decreased from 17.4 to 9.3 Ω/sq. From the Raman spectrum in Figure 1d, three prominent peaks with the D peak, G peak, and 2D peak were observed. The D peak at ∼1350 cm−1 induced by defects, the G peak at ∼1580 cm−1 resulting from the doubly degenerate zone center E2g mode, and the sharp 2D peak at ∼2700 cm−1 originating from second-order zone-boundary phonons indicated the existence of graphene after the laser pyrolysis process. As shown in the high-resolution transmission electron microscopy (TEM) image of LIG (Figure S4), the average lattice space is about 0.337 nm, corresponding to the (002) planes in graphitic materials. From the TEM selected area electron diffraction (SAED) pattern, the (002) planes were also observed, indicating the formation of graphene sheets.

The elemental composition and concentration of LIG were investigated by X-ray photoelectron spectroscopy (XPS). In the survey spectrum (Figure 1e), the elements C and O could be observed. The binding energy values of C 1s and O 1s for the sample were found to be 284.8 and 532.8 eV, respectively. The results obtained showed that the molar ratio of C/O is close to 11:1. The high-resolution C 1s XPS image of LIG further indicated that LIG contained sp2 carbons with C−C peak being dominant at 284.5 eV (Figure 1f). For the high-resolution O 1s XPS image of LIG (Figure 1g), a broad peak appeared at 532.3 eV, indicating the combination of C−O (533.2 eV) and C=O (531.8 eV) bonds, which is in agreement with the results previously reported.

To verify the feasibility of an in-series structure for MSCs, MSCs with output voltage ranging from 1 to 6 V were fabricated, as schematically shown in Figure 2a. Two symmetric electrodes separated by a gap were denoted as one unit of an MSC. The gap between two electrodes was coated with the H2SO4−PVA electrolyte, leading to 1 V output for each unit. When three or six units are connected in series, MSCs with 3 or 6 V outputs, respectively, can be constructed. In fact, the voltage output scales linearly with the number of units of MSCs. The capacitance of a symmetric supercapacitor cell (Cdevice) can be estimated by the CV curves using eq 1:

\[
C = \frac{Q}{V} = \frac{1}{2V} \int_{-V/2}^{V/2} i(V) dV
\]

where Q is the total charge obtained by integration of the CV curve, i is the current, v is the scan rate, and V is the potential window. The CV curves of the three different devices (1, 3, 6 V).
and 6 V) under a scan rate of 100 mV/s showed capacitances of 58.1, 20.4, and 11.3 \(\mu F\), respectively (Figure 2b), demonstrating the feasibility of the in-series structure for high-voltage planar MSCs.

The galvanostatic charge−discharge method was used to accurately characterize the capacitive properties of these MSCs. The capacitance could be calculated from the following equation \(C = \frac{I \times t}{V}\) (2)

where \(I\) is the applied current, \(t\) is the discharge time of the supercapacitors, and \(V\) is the electrochemical potential window.

For conventional capacitors, it is well known that the in-series connections would result in the decay of capacitance. Supercapacitors also behave in a similar manner. The total capacitance of a high-voltage MSC connected in series could be calculated as

\[
\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \cdots + \frac{1}{C_n} = \sum_{i=1}^{n} \left(\frac{1}{C_i}\right)
\]

where \(C\) is the total capacitance of a high-voltage MSC and \(C_i\) is the capacitance of each unit. For first-order approximation, \(C_1 = C_2 = C_3 = C_n\) and this results in \(C = C_1/n\). After calculating the charged and discharged results from Figure 2c, the capacitances for 1, 3, and 6 V MSCs were 60.5, 20.7, and 10.0 \(\mu F\), respectively, under an applied current of 1.0 \(\mu A\).

Supercapacitors typically have excellent cycling stability; however, little is known about the cycling stability of high-voltage MSCs with an in-series electrode architecture. To shed light on this crucial characteristic, a 5000-cycle charge−discharge test was conducted for a 6 V MSC, as shown in Figure 2d, and the 6 V MSC retained about 97.8% of the initial capacitance. The inset shows charged−discharged profiles of the last 10 cycles in a 5000-cycle test. The capacitance decay could possibly be attributed to the tiny variations of voltages that exist among different units, a result of the electrolyte coating process that could be further improved and optimized.
A digital image of a 209 V all-solid-state flexible MSC is shown in Figure 3a. As shown in Figure 3b, one corner of the 209 V MSC was clearly observed with the uniform coating of H$_2$SO$_4$–PVA electrolyte. To demonstrate the flexibility of the high-voltage MSCs, as shown in Figure 3c, a flexible planar 209 V device was tested with negligible degradation of charge and discharge curves at 2.0 μA when it was bent at different angles ranging from 0 to 180°, showing the good stability of the planar high-voltage MSC. Instead of comparing the areal or volumetric capacitances between MSCs with different output voltages, we use the capacitance derived from the designed MSC with a specific geometry. The volume of the 209 V MSC device is calculated to be 0.3 cm$^3$ (Figure S5). Figure 3d–f shows the CV curves and the corresponding capacitance of the 209 V device. The rectangular and symmetric shapes of the CV curves indicated their capacitive properties with scan rates ranging from 0.1 to 10 V/s. The 209 V MSC was able to achieve 0.37 μF at 0.1 V/s when it was discharged from 209 to 0 V and 0.19 μF at a scan rate of 10 V/s. The charged and discharged data (Figure 3g–i) were further used to evaluate the performance of the 209 V device with various applied currents ranging from 0.2 to 5.0 μA. It can be seen that the all-solid-state 209 V MSC could achieve a high capacitance of 0.43 μF at a low applied current of 0.2 μA and a capacitance of 0.18 μF even at a high applied current of 5.0 μA. These charge curves are relatively symmetric to their corresponding discharge counterparts at different applied currents, further revealing the capacitive behavior of the flexible all-solid-state 209 V MSC. The maximum specific volumetric capacitance of the 209 V device was calculated from the charged–discharged curve to be 1.43 μF/cm$^3$, which was comparable to the value (10.0 μF/cm$^3$) of a commercial ceramic capacitor (X7R 1210) and 24 times larger than the value (0.06 μF/cm$^3$) of a commercial Panasonic thin-film capacitor (Table S1). Meanwhile, the 209 V MSC also maintained excellent flexibility compared to the fragile ceramic capacitor. For the microsupercapacitors, they are often characterized and compared by using the volumetric energy density instead of the mass-based
energy density because the mass of the active materials was tiny. The volumetric energy density was calculated based on the following equation: 

\[ E = \frac{1}{2}CU^2/V \]

where \( C \) is the device capacitance of the 209 V MSC, \( U \) is the working voltage of the device, and \( V \) is the volume of the 209 V MSCs. Therefore, the volumetric energy density of 209 V MSCs was calculated as 31.3 mWh/cm\(^3\) at 0.67 \( \mu \)A/cm\(^3\), which was much larger than the capacitance (5.7 mWh/cm\(^3\)) from the previous work of microsupercapacitors based on laser-processed graphene.

The electrochemical impedance spectroscopy test was conducted in a frequency range of 1 Hz to 1 MHz to further evaluate the electrochemical behaviors of the 209 V solid-state microsupercapacitor. As shown in the Nyquist plots in Figure S9a, the intercept of the Nyquist curve on the real axis was about 13.7 k\( \Omega \), indicating reasonable conductivity of the solid-state electrolyte and internal resistance of the device. The semicircle diameter referring to the charge-transfer resistance (\( R_{ct} \)) was about 529 k\( \Omega \), which was acceptable for the high-voltage microsupercapacitors usually working in the \( \mu \)A current ranges. Moreover, the Bode plot is also recorded in Figure S9b, and it is be observed that the capacitor response frequency (\( f_0 \)) at the phase angle of \(-45^\circ\) was 4.64 Hz, which was similar to the values of solid-state supercapacitors based on carbon nanoparticles/MnO\(_2\). The corresponding time constant \( \tau_0 \) (=1/\( f_0 \)) was 216 ms, which was close to that of laser-scribed graphene supercapacitors (33 ms) but much shorter than that of supercapacitors based on activated carbon (in the range of 10 s). The phase angle of the 209 V MSC was about \(-77^\circ\) at a frequency of 1 Hz, which is close to \(-90^\circ\) for ideal capacitors.

To demonstrate the potential of these high-voltage MSCs, a 6 V MSC was used to drive a wearable piezoresistive pressure sensor (Figure 4a), which was made by transferring the LIG onto a polydimethylsiloxane (PDMS) substrate based on a modified process from a previous report (see Figure S13). Briefly, a serpentine-shaped LIG was directly laser-written on Kapton substrate. Next, liquid PDMS was poured onto the patterns. After heating for 2 h in an oven, the serpentine LIG was transferred onto the curing PDMS. To prevent possible contact with moisture, the surface of LIG was covered by another layer of PDMS.

Figure 4c shows the responses of the microsensor under an applied voltage of 6 V powered by a Gamry workstation while being finger-pressed at a pressure of about 60 kPa (Figure 4b) manually. The deformation of the sensor caused the increase in resistance and reduction in measured current as shown. The detailed signals were zoomed in the inset, and some variations were observed due to the manual pressing operations. When the power source was replaced by using a 6 V MSC, very similar data could be obtained in Figure 4d. However, the baseline of current gradually decreased with time because of the continuous decrease of the supplied voltage from the 6 V MSC due to both the leakage and consumption of charges during the operations. The microsensor was further placed under an insole inside a running shoe to monitor the ambulatory motions in Figure 4e. By using the Gamry workstation as a power source with 6 V output, a highly stable \( I-t \) curve could be achieved, as the microsensor recorded the heel strikes during 1 min of walking (Figure 4f). After replacing the power source by a 6 V MSC, a similar \( I-t \) curve (Figure 4g) with a constant decrease of baseline current was observed, indicating excellent performance of the flexible planar high-voltage MSCs. The zoomed-in signals were nearly the same from two different power sources, validating the robustness and feasibility of our MSCs.

Figure 5a shows the detailed structure of a crawling robot, which was a 20 mm long and 47 mg weight prototype. The cantilever beams together with the additional mass can be excited to vibrate back and forth by a high-voltage direct-current power source (>2000 V) to impact the electrodes in sequence and achieve self-sustained walking gaits, according to previous reports. To demonstrate the feasibility of the high-voltage MSC, the walking robot was driven by 10 in-series-
connected 209 V MSCs, as shown in Figure 5b. The crawling movement of a walking robot powered by a 2090 V MSC stack for 11 s was recorded by a digital camera from Figure 5c,5d. These results proved that high-voltage MSCs with planar in-series structure could be a good option among energy-storage devices.

**CONCLUSIONS**

In conclusion, this work reports a high-voltage flexible planar MSC with an in-series LIG electrode architecture via direct laser engraving of polyimide film. The high-voltage all-solid-state MSCs were flexible and capable of supplying output voltages ranging from a few to thousands of volts. We demonstrated the robust function of our flexible high-voltage MSCs by using them to power a piezoresistive microsensor that was designed as a wearable step counter to track walking activities. Besides, a walking robot was also successfully powered by a 2090 V MSC stack for 11 s. Considering the simple, direct, and cost-effective fabrication method of our laser-patterned high-voltage flexible planar MSCs, this work paves the way and lays the foundation for high-voltage energy-storage devices.

**METHODS**

**Fabrication of the 209 V MSC.** Kapton polyimide film (McMaster-Carr; Cat. No. 2271K3; thickness: 125 μm) was used in this work. The CO2 laser (wavelength, 10.6 μm) with an optimized scan rate of 250 mm/s and an output power of 8.0 W was used to heat the Kapton film with designed 210 sq. For each square electrode, the side length was 3.0 mm with a gap of 500 μm between every two electrodes. After the laser-heating process, the gaps were brush-coated by electrolyte, leaving approximately 40% of each LIG square without the coating of the electrode as the common conductive electrode for in-series connection. The electrolyte was made by adding 1.0 g of PVA (Mw: 89 000−98 000) into 5.0 mL of 1.0 M H2SO4 solution, which was subsequently heated at 95 °C for 20 min until the solution turned clear.

**Fabrication of the Pressure Microsensor.** The Kapton film was laser-heated into a conductive serpentine-shaped LIG first. After the laser-heating process, PDMS (Sylgard 184, Dow Corning, mixing ratio 1:1) was cast onto the LIG patterns. To remove the air from the small pores inside the porous graphene networks and allow the full penetration of PDMS liquids, a vacuum step was necessary. The laser-heated PDMS/LIG microsensor was peeled off from the Kapton film and further covered by another layer of PDMS.

**Characterizations.** The electrochemical performances of 1, 3, and 6 V MSC were measured by an electrochemical workstation (Gamry Reference 600 potentiostat). The 209 V MSC was tested by Keithley 2400. The I−I curves for the microsensors were obtained from the Gamry workstation with a sample period time of 0.001 s. SEM images were taken with an FEI Quanta three-dimensional scanning electron microscope. The transmission electron microscopy (TEM) image and the SAED pattern were recorded on an FEI Titan 80−8300. XPS investigations were conducted on a PHI 5600 X-ray photoelectron spectrometer. Raman spectra were recorded on LabRAM Aramis (HJY, France). The shear viscosity of electrolyte was characterized by Anton Paar at 25 °C.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b10301.

Schematic calculation of electrolyte-covered area; shear viscosity of electrolyte; digital image of a tiny brush; TEM image of LIG; comparison of the high-voltage planar MSC with commercial capacitors (PDF)

**Bending test of the 209 V MSC (Video S1) (AVI)**

Walking robot (Video S2) (AVI)

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**Notes**

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**REFERENCES**


