A 1000-VOLT PLANAR MICRO-SUPERCAPACITOR BY DIRECT-WRITE LASER ENGRAVING OF POLYMERS

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ABSTRACT

A 1000V, high-voltage planar micro-supercapacitor directly fabricated on a flexible polymer substrate has been demonstrated to successfully power an electrostatic cantilever microresonator for more than 1 minute. Direct-write laser engraving of Kapton tape (polyimide) was used to fabricate each 200V micro-supercapacitor rapidly in a single step at ambient condition for the first time. To actuate the microresonator, five 200V micro-supercapacitors were connected in series to attain a 1000V output in a stable and safe manner. We demonstrated that laser engraving is a highly feasible and cost-effective technique for fabricating very high-voltage energy storage devices that are portable, flexible, and lightweight.

INTRODUCTION

Supercapacitors, also known as electric double-layer capacitors (EDLC) or ultracapacitors, store charges via the adsorption and desorption of ions within the electrical double layer that exists between the solid electrodes and the bulk electrolytes. Since the ions can rapidly desorb from the surface of the electrodes, supercapacitors are able to release power in a short time, giving rise to high power density [1]. Typically, supercapacitors are capable of delivering a power density that is an order of magnitude (10 $kWkg^{-1}$) larger than that of lithium ion batteries [2]. Thus, supercapacitors are good complements to batteries, which typically have high energy density but significantly lower power density. Carbon-based materials such as graphene are commonly used as the electrodes for supercapacitors because carbon are abundant, inexpensive and has an excellent cycle life [3]. Many allotropes of carbon or carbon-based nano-materials have previously been designed for the state-of-the-art supercapacitors. These includes onion-like carbon [4], carbide-derived carbon [5], nitrogen-doped graphene [6], carbon nanotubes [7], and laser scribed graphene [8].

To date, micro-supercapacitors have been researched extensively for use in miniature electronics because they could act as an excellent complementary power source to batteries in a variety of applications including sensors and actuators [9, 10]. Recently, Wu et al. reported a high-power density and high-energy density graphene-based micro-supercapacitor capable of outputting a power density of $495Wcm^{-3}$ [11]. Nevertheless, the lithography process and the high-temperature post-fabrication heat treatment made the patterning of micro-supercapacitors complicated and time-consuming, unnecessarily increasing the cost of the micro-supercapacitor. Compared to lithographic process that involves multiple masking steps, direct laser writing of micro-supercapacitors provides a less-process intensive fabrication route that enables substantially faster design iterations. Back in 2011, Gao et al. reported a direct laser writing technique to make micro-supercapacitors based on laser reduced graphene oxide [12]. It is, however, widely known that the production of graphene oxide yields toxic chemical wastes that include strong acid (H_2SO_4) and toxic gas (NO_2) [13]. To circumvent the issue of toxic byproducts, Lin et al. used direct laser writing on commercial polyimide to develop a graphene micro-supercapacitor capable of achieving specific capacitance of $44mF\text{-}cm^{-2}$ and power densities of $9mW\text{-}cm^{-2}$ [14]. Despite such progress, however, it remains a critical challenge to fabricate micro-supercapacitors that could produce high voltages for various potential applications in sensors and actuators.

This work explores the use of a laser engraving fabrication technique to enable the design and rapid fabrication high-voltage (up to 1000V) micro-supercapacitors at ambient condition and in an environmentally friendly manner. In our process, an infrared laser directly and rapidly pyrolyzes polyimide into highly conductive graphene electrodes for micro-supercapacitors. By judiciously adjusting laser power and scan rate, one can easily custom-design and directly laser-write micro-supercapacitor arrays capable of outputting voltages between 1-1000V via series connections. Our device has been demonstrated to power an electrostatic cantilever resonator which needs a high voltage (about 1000V) to actuate [15]. Compared with prior fiber-shaped high-voltage micro-supercapacitors [16], the direct-write technique is more controllable and convenient. The approach we claimed here provides a unique way to design and fabricate portable and lightweight high-voltage energy storage devices.

SETUP AND MATERIALS

Materials Preparation

Poly(vinyl alcohol) (PVA, Mw: 89,000-98,000) and sulfuric acid (98%) were purchased from Sigma-Aldrich and used without further purification or modification. Nulink™ Kapton tape was purchased from Amazon online website and used without further purification or modification. The electrolyte, H_2SO_4-PVA, was prepared by adding 1.0 g of PVA into 5.0 ml of 1.0 M H_2SO_4 solution, which was subsequently heated at 95 ºC for 20 minutes until the solution turned clear.

Experimental Details

Figure 1 illustrates the process of making the 200-Volt micro-supercapacitor using a CO_2 infrared laser (10.6 μm in wavelength), whose optimal scan speed and output power were 250 mm/s and 4.0 Watt, respectively. Briefly, a programmable software was utilized to design the 200V micro-supercapacitor array, which was subsequently patterned on the Kapton film via a pyrolysis process. Immediately upon transient laser heating, the surface of the pyrolyzed Kapton (polyimide) tape transformed into a micro- and macroporous graphene/graphitic network, which exhibits superior physical and electrical characteristics for potential energy storage applications. Each array contained 200 pairs of electrodes (anodes and cathodes) connected in series, and each pair of electrodes was separated by a gap of 500μm that was later filled with 1.0 M H_2SO_4-PVA electrolyte. The inset image shows an optical micrograph of one corner of the pyrolyzed micro-supercapacitor array. Furthermore, an SEM image illustrates the porous morphology of the as-prepared graphene patterns, which display high surface area for charge storage and therefore potentially excellent electrochemical storage.

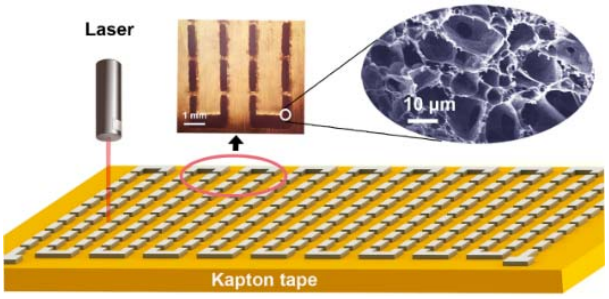

Figure 1: (a) Schematic of the laser engraving of Kapton tape with the laser scan speed of 250 mm/s and laser power output of 4.0 Watt. Scale bar are 1mm and 10 μm for the (b) optical image and (c) the SEM image, respectively.

RESULTS RESULTS AND DISCUSSION

Figure 2 shows the measurement method for the sheet resistance of the laser engraved graphene film. The two-point probe method measures the sum of resistances of the film, wires, and contacts, so the material should be significantly more resistive than the wires and contacts. And for the four-point probe method, it is suitable for materials with higher conductivity because it eliminates the resistance of the contacts and wires. For the highly conductive graphene film, it's better to choose the four-point probe method to measure the resistance of the materials. The resistance (R) of a material could be written as follows:

$$\mathrm{R} = \rho\frac{L}{A} = \rho\frac{L}{WT} = \frac{\rho}{T}\frac{L}{W} = R_S\frac{L}{W}$$

Where L is the length, A is the cross-sectional area of the film and ρ is the bulk resistivity. The cross-sectional area is the product of the width (W) and the sheet thickness (T). Rs is the sheet resistance of the film.

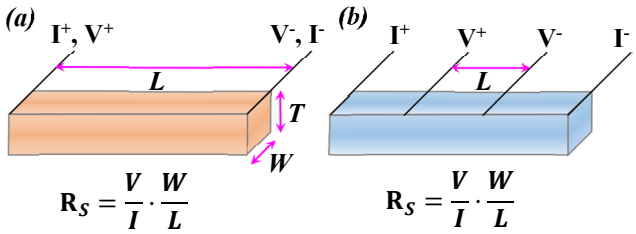

Figure 2: Two methods for measuring sheet resistances of the laser-engraved graphene films. (a) Two-point probe measurement; (b) Four-point probe measurement.

In the real measurement of the laser-engraved graphene film, we designed a square for the sheet resistance measurement. Since the length L is equal to the width W, Rs is equal to R.

As shown in Figure 3, when the power of the laser was set at 4.0 Watt, with the increase of the laser scan speed from 150 mm/s to 400 mm/s, the sheet resistance of graphene film increased from 11.1 Ω/square to 32.8 Ω/square. While higher laser scan speed denoted higher production rate, the short resident time of the laser beam might not have completely converted polyimide into graphene, leaving behind residual polyimide, which is electrically insulating. This observation was manifested in the higher sheet resistances as scan rate increased. In order to achieve a balance between conductivity of the film and production rate, we used a laser scan rate of 250 mm/s which yielded a sheet resistance of 17.3Ω/square for our specimens.

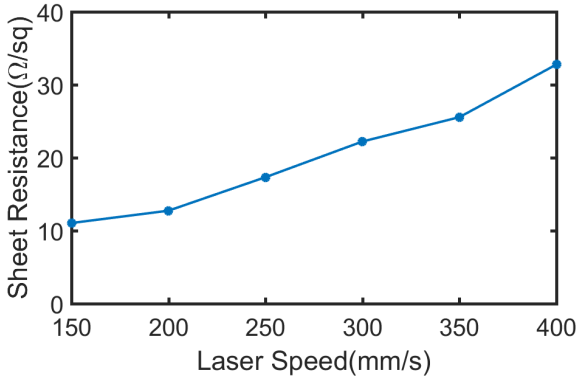

Figure 3: Correlations of the sheet resistance and the laser scan speed from 150 mm/s to 400 mm/s at a constant laser power of 4.0 Watt.

In order to verify the possibility of an in-series micro-supercapacitor structure, we first fabricated 1V, 2V, and 3V micro-supercapacitors. Figure 4(a) shows the schematic structures with different output voltages ranging from 1V to 3V. Two electrodes—an anode and a cathode—are denoted as one unit of a micro-supercapacitor and the gap between the two electrodes is coated with solid-state H_2SO_4-PVA electrolyte, leading to 1V output for each unit. When two or three units are connected in series, micro-supercapacitors with 2V or 3V outputs, respectively, can be constructed. In fact, the voltage output of a micro-supercapacitor constructed this way scales with the number

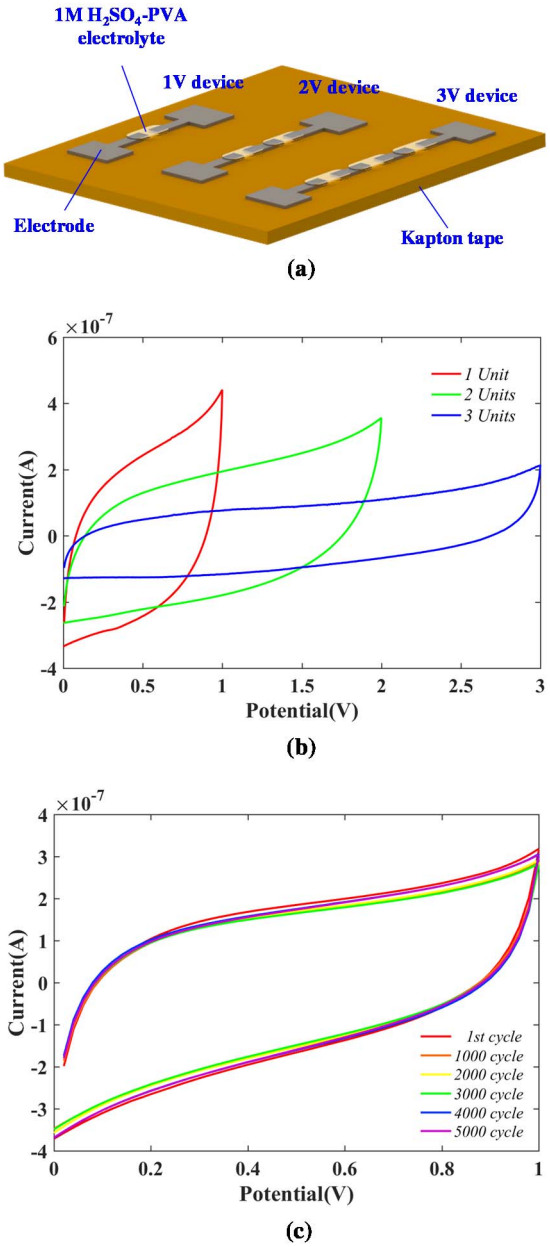

Figure 4: (a) The schematic structure with different output voltages of 1V, 2V, and 3V. (b) The cyclic voltammetry (CV) curves of the three devices (1V, 2V and 3V) at a scan rate of 100mV/s. (c) The CV curves of the 1V-device tested after 1, 1000, 2000, 3000, 4000, and 5000 cycles.

of units of micro-supercapacitor, can be easily customized. Cyclic voltammetry (CV) is an electrochemical technique which measures the current while cycling the potential of a working electrode in a three-electrode electrolytic cell. The capacitance of a symmetric supercapacitor cell (C_{device}) canbe estimated by CV curves using the following equation:

$$C_{device} = \frac{Q}{V} = \frac{1}{2Vv}\int_{V-}^{V+} i(V)dV$$

Where Q is the total charge obtained by integration of the CV curve, i is the current, v is the scan rate, V is the potential window. The cyclic voltammetry (CV) curves of the three different devices (1V, 2V and 3V) at a scan rate

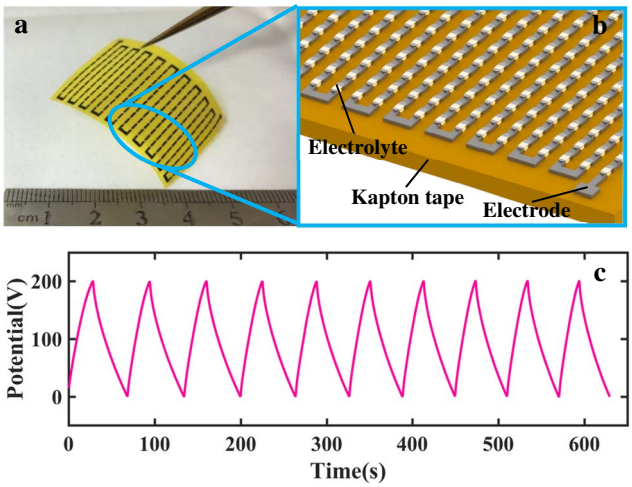

Figure 5: (a) Digital image of the as-prepared 200V device. (b) Schematic view of the device with 200 units coated by electrolyte and connected in series. (c) Galvanostatic charge/discharge (CC) curves for the 200V device

of 100mV/s display specific capacitance of 2.1 µF, 1.6 µF and 0.9 µF, respectively, as shown in Figure 4(b). In addition to capacitance, cycling stability of the 1V-device is another critical performance parameter of the micro-supercapacitor. The 1V device was electrochemically cycled for more than 5000 times to examine any resulting degradation. Figure 4(c) showed the remarkable stability of the device with negligible change in capacitance.

A digital image of the as-prepared 200V-device with 200 units coated by electrolyte and connected in series is shown in Figure 5(a) and the detailed cell structure in Figure 5b. Galvanostatic charge/discharge behaviors could be used to characterize the electrochemical properties of these supercapacitors. The capacitance could be calculated from the following equation:

$$C_{device} = \frac{It}{V}$$

Where I is the applied current, t is the discharge time of the supercapacitors and V is the electrochemical potential windows.

Figure 5(c) shows that the 200V-device at an applied current of 0.2 µA achieved a capacitance of 40 nF as calculated from the galvanostatic charge/discharge (CC) curves. The symmetry of the charge-discharge curves indicated outstanding electrochemical performance of the micro-supercapacitor array with 200 units connected in series.

Figure 6(a) illustrates a schematic of the real application of the high-voltage micro-supercapacitor array, in which an electrostatic cantilever resonator is powered in by a 1000V micro-supercapacitor array made up of five 200V devices connected in-series. Figure 6(b) shows the actual micro-supercapacitor array connected to the resonator. In order to make visible the oscillation of the cantilever resonator during operation, a red flag is attached to the end of the beam and a high-speed camera is used to capture the movements of the cantilever resonator at every 0.025 seconds (Figure 6(c)). The resonator keeps oscillating for one more minute which shows our micro-supercapacitor is able to store an adequate amount of charges.

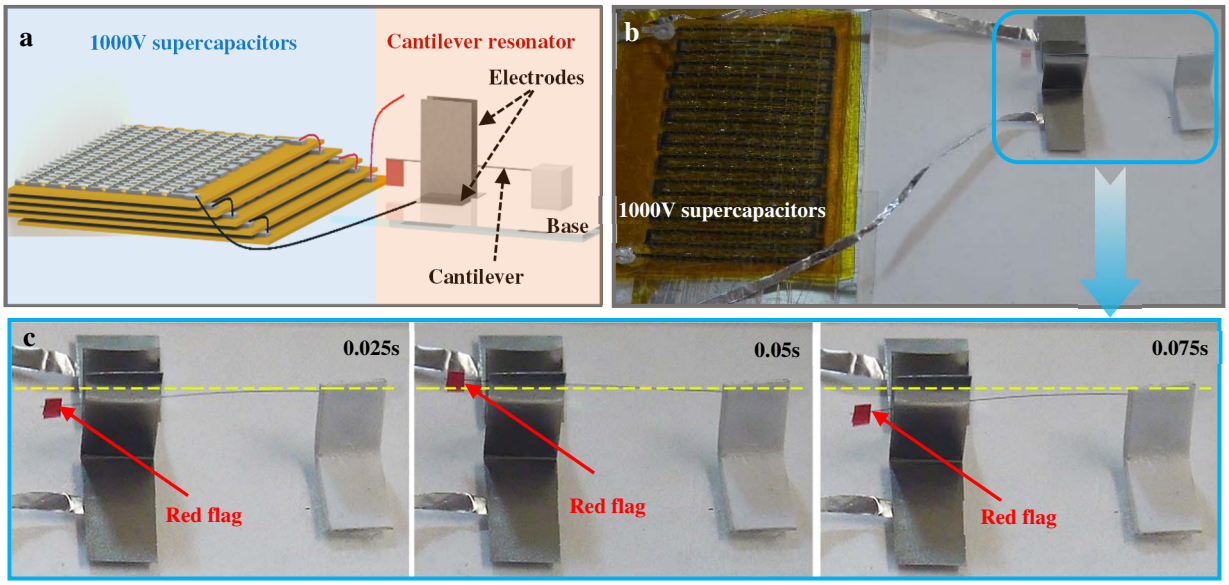

Figure 6: A cantilever resonator to demonstrate a real application of the high-voltage micro-supercapacitors. (a) Schematic diagram and (b) digital picture of a cantilever resonator powered by a 1000V micro-supercapacitor array; (c) The movement of the vibrating cantilever resonator recorded at every 0.025 seconds

CONCLUSION

In summary, we have developed a technique based on laser engraving of polyimide to fabricate a 1000V micro-supercapacitor array capable of powering a cantilever resonator for up to 1 minute. Using direct-write laser engraving, Kapton tape (polyimide) can be pyrolyzed and instantaneously transformed into highly conductive graphene electrodes at ambient conditions. In conclusion, we have capitalized on a laser engraving technique to create an innovative means to fabricate portable, lightweight and low-cost high-voltage energy storage devices for various applications.

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