ABSTRACT
This paper reports a simple and scalable technique for the fabrication of flexible micro-supercapacitors. The supercapacitor electrodes are synthesized via the pyrolysis of patterned photoresist on a SiO₂/Si substrate. The electrodes can then be moved to flexible substrates through a simple transfer process. The fabricated devices show excellent energy density of 0.3 mJ/cm², maximum power density of 5 mW/cm², and good performance under electrochemical cycling. The electrochemical performance is maintained after 300 mechanical bending cycles.

INTRODUCTION
Supercapacitors are energy storage devices that have high power density and more robust cycle lifetime relative to existing battery technologies [1, 2, 3]. These properties make microscale supercapacitors attractive for integration in applications such as mobile or autonomous microdevices. In particular, flexible micro-supercapacitors have received increasing research interest for applications including bioimplantable devices, flexible displays, and wearable electronics. In these applications, an integrated flexible energy storage device is necessary for maintaining device mobility, flexibility, and small form factors.

Supercapacitors are composed of two primary components, the two electrodes and the electrolyte. In order to store charge, the electrodes are polarized by an external voltage, and the mobile ions in the electrolyte preferentially migrate to form areas of high charge density at each electrode/electrolyte interface. Due to this interfacial electrostatic charge storage mechanism, supercapacitor electrodes must have extremely high surface area in order to store appreciable amounts of energy. Furthermore, electrode materials should have sufficient electrical conductivity in order to transport charge carriers without excessive resistance. In addition to these requirements of high surface area and good conductivity, microscale supercapacitor electrodes must also be easily deposited and patternable. For these reasons, photoresist-derived porous carbon is a promising material for micro-supercapacitors due to its porosity, good conductivity, and easy patternability [4, 5, 6].

While the electrochemical performance of this material has been successfully demonstrated on rigid substrates [4, 5], for incorporation into flexible devices, the porous carbon structures must be successfully transferred onto flexible substrates. This paper reports the fabrication and testing of devices fabricated from the transfer of patterned porous carbon structures.

METHODS
The fabrication of the micro-supercapacitor is illustrated schematically in Figure 1. First, the photoresist is patterned into a two-pad electrode configuration on a SiO₂/Si substrate. The sample is then pyrolyzed at 900 °C in a hot wall tube furnace in H₂ and Ar as described in Ref. [4]. A double-transfer technique is then used to transfer the patterned electrodes to a flexible substrate. First, a polycarbonate sheet is adhered to the sample upon heating to 300 °C. After cooling, the sheet is carefully peeled off from the substrate; the porous carbon preferentially adheres to the polycarbonate, transferring the patterned electrodes. As will be further discussed, this single transfer inverts the carbon electrodes, exposing the surface of the film that was in contact with the SiO₂ during pyrolysis, and yields a lower capacitance than the untransferred electrodes. Therefore, a second transfer is needed. This transfer is performed by adhering a polyethylene sheet to the polycarbonate at 200 °C and selectively etching the polycarbonate in methylene chloride.

The morphology of both surfaces of the film is probed via atomic force microscopy (AFM, Digital Instruments Nanoscope IIIa) in tapping mode. In order to test the electrochemical performance of the device, Cu tape is used to make electrical connection to the electrodes and a 0.5 M H₂SO₄ aqueous solution is used as the electrolyte. Cyclic voltammetry (CV), galvanostatic charge/discharge, and AC impedance (AC Instruments, 660D Model) are used to probe the electrochemical characteristics of the fabricated device.

Figure 1: Schematic of flexible microsupercapacitor fabrication
RESULTS AND DISCUSSION

Comparison between Electrode Top and Bottom Surfaces

As previously mentioned, the morphological and electrochemical properties of the pyrolyzed photoresist surface are significantly different for the untransferred and singly transferred films. These differences arise during the pyrolysis process. The “top” surface of the photoresist is exposed to the H2/Ar ambient during pyrolysis, while the “bottom” surface is in contact with the underlying SiO2 layer on the substrate. The first transfer exposes the bottom surface to the electrolyte and thus shows different electrochemical behavior.

The AFM results (shown in Figure 2) show that the top surface is significantly rougher than the bottom surface. The RMS roughness is calculated to be about 1.3 and < 0.3 nm, respectively. This difference in surface morphology likely results from three factors. First, the bottom surface of the photoresist is in contact with the smooth thermal oxide surface and forms a matching smooth surface. Second, the pore formation mechanism during pyrolysis stems from the evaporation of volatile components from the film and this evaporation occurs through the top surface [7]. Third, pore formation and accessibility are assisted through a hydrogen etching process which occurs primarily at the top surface due to transport limitations [4, 7].

These morphological differences are manifested in the electrochemical testing of the films after one transfer and after a second transfer (which recovers the original top surface). CV tests show that devices fabricated after one transfer give areal capacitances of only 10 µF/cm² at a scan rate of 100 mV/s (all values normalized by the projected active area of both electrodes), while devices fabricated after the second transfer give capacitances about 75 times higher at the same scan rate, 0.75 mF/cm². Thus, a double transfer appears to be necessary to achieve high energy density devices.

Electrochemical Analysis

Cyclic voltammetry scans of the device show near-ideal electrochemical behavior at scan rates of up to 10 V/s, as evidenced by the rectangular CV plots shown in Figure 3.

The specific capacitance, $C$, achieved for the device is calculated via Equation 1,

$$C = \frac{I_{avg}}{sA}$$

where $I_{avg}$ is the current averaged over both positive and negative sweeps, $s$ is the scan rate, and $A$ is the projected area of both electrodes which is in contact with electrolyte. $C$ is calculated to be 0.75 mF/cm² at a scan rate of 100 mV/s, dropping to 0.62 and 0.36 mF/cm² at 1 and 10 V/s respectively. These values correspond to a material capacitance of between 1.4 and 3 mF/cm² which is calculated by multiplying the device specific capacitance by a factor of 2 to obtain the capacitance at one electrode and by another factor of 2 to normalize by active area of one electrode. These results show good agreement with Ref. [4] which shows a specific capacitance of 1.5 – 3.5 mF/cm² for three-electrode measurements on an unpatterned pyrolyzed film.

Galvanostatic charge/discharge tests also show near ideal capacitive performance, with linear charge and discharge curves at all probed scan rates. Three representative curves are shown in Figure 4a. A small IR drop is present in each discharge curve, indicating some ohmic resistance in the device, known as the equivalent series resistance (ESR). The ESR can be calculated via Equation 2,

$$ESR = \frac{V_{drop}}{2I}$$

where $V_{drop}$ is the magnitude of the IR drop and $I$ is the applied current density. The ESR is about 8 Ω·cm² for the device. This ESR limits the maximum power and probably arises from the high resistance of the carbon film and the contact resistance to the Cu tape current collector.
AC impedance tests also show typical supercapacitor behavior, with a near-vertical line in the Nyquist plot [2, 8] (Figure 4b). The AC frequency at which the phase shift crosses ~45° is ~122 Hz for the fabricated device. This value indicates the approximate highest frequency at which the device can yield capacitive behavior and compares favorably to other flexible micro-supercapacitors such as laser-scribed graphene based devices, which show a crossover frequency of about 50 Hz [9].

Cycle lifetime studies are performed through 10,000 repetitive CV cycles at a scan rate of 100 mV/s. The good capacitive performance of the device is maintained throughout the cycling, with a capacitance retention of 86%.

Energy and Power Density
The primary figures of merit for supercapacitors are the energy and power density. For microscale devices, the areal and volumetric densities are most frequently reported (rather than the gravimetric density). The energy density, $E$, and power density, $P$, are calculated from Equations 3 and 4,

$$E = \frac{1}{2} CV^2$$

$$P = \frac{\Delta E}{\Delta t}$$

where $C$ is the specific capacitance calculated from $CV$, $V$ is the voltage window over which the device is cycled (0.8 V in this case), and $\Delta t$ is the discharge time. Many CV scan rates are tested, yielding several points on the Ragone plot as plotted in Figure 5. Volumetric densities can easily be calculated by dividing the areal values by the film thickness (0.9 µm). The energy density achieved is extremely high, $10^{-8}$ to $10^{-7}$ Wh/cm$^2$ (0.05 to 0.3 mJ/cm$^2$) or $10^{-4}$ to $10^{-3}$ Wh/cm$^3$ (0.6 to 3.5 J/cm$^3$). For comparison, laser-scribed graphene based flexible micro-supercapacitors yield about $2 \times 10^{-4}$ to $5 \times 10^{-4}$ Wh/cm$^3$ energy density using an aqueous gel electrolyte [9]. These comparison values are obtained by normalizing by device area, rather than electrode area, as in this work, so the actual energy density of the electrode material is slightly underestimated for the laser-scribed graphene. Nonetheless, the energy densities achieved in this work are competitive with state-of-the-art flexible electrode materials.

Flexibility Testing
In order to probe the performance of the device under flexion, the $1 \times 1$ cm$^2$ sample is conformally wrapped around cylinders of various size and manually cycled from an unbent to a bent position. This cycle is repeated 100 times for a 17.5 mm radius of curvature. The device is then tested in an unbent configuration. The bending cycle is then repeated 100 more times for $r = 12.5$ mm, and the device is tested again. Finally, 100 more cycles are performed at $r = 5$ mm. Figure 6 shows the CV results before and after each 100 cycle test. The difference in initial capacitance and capacitance after mechanical cycling is ~ 2%. This excellent retention of capacitance indicates that the pyrolyzed photoresist electrodes can withstand repeated flexing cycles and that this material is promising for integration in flexible energy storage applications.
CONCLUSION

In summary, this work presents a scalable and simple technique to fabricate and transfer micro-supercapacitor electrodes for flexible microscale energy storage applications. The electrode material, pyrolyzed photoresist, is a promising material micro-supercapacitor material platform due to its high specific capacitance, good conductivity, and easy large-scale manufacturability. A double-transfer to a flexible substrate is necessary for achieving good capacitive performance and very high energy densities. Both the electrochemical and mechanical stability of the device is excellent. This fabrication technique is a promising step towards flexible microscale integrated energy storage devices.

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