Origami fabrication of nanostructured, three-dimensional devices: Electrochemical capacitors with carbon electrodes

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The Nanostructured Origami™ process consists of patterning a two-dimensional (2-D) membrane with desired micro- and nanoscale features and then folding it into a three-dimensional (3-D) configuration. Electrochemical capacitors, or supercapacitors, are ideal for origami fabrication because their performance can be enhanced through the use of 3-D geometry and nanostructured materials. A supercapacitor with an electrode area of 350 × 350 μm was created using the origami process and characterized using electrochemical analysis methods. The experimentally measured capacitance values of approximately 1 μF are consistent with theoretical predictions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2177639]

The Nanostructured Origami™ 3-D Fabrication and Assembly Process, inspired by the paper folding art of origami, is a two-step fabrication approach that combines established microfabrication tools with state-of-the-art nanofabrication techniques to create 3-D devices with nanostructured materials. In the first step of the process, standard planar fabrication tools and techniques are used to create a micro- and nanopatterned 2-D membrane. The membrane can be thought of as the analog of “paper” used in conventional origami and, in addition to being patterned directly, can provide a base on which to grow or deposit nanostructured materials. During this stage, the membrane is also patterned with features that will allow it to fold, such as creases, hinges, and various actuation mechanisms. In the second step of the origami process, the membrane is automatically folded into the desired 3-D configuration. Automatic folding, an important feature of the origami process that enables batch fabrication, has been accomplished previously through either Lorentz force or strain-induced actuation methods. Membrane folding of up to 180° was achieved using either method.

The Nanostructured Origami™ process provides several advantages over current fabrication methods. First, a multilayer device can be made by patterning and repeatedly folding a single layer. Because only one layer needs to be patterned, fabrication difficulties associated with multilayer devices can be avoided. Improved alignment and spacing (~1 μm) among the folded layers can be achieved through the use of pyramid-shaped alignment features. In addition, whereas current nanofabrication methods are largely limited to building nanostructures on the top surface of a horizontally oriented substrate, the origami method allows the patterned surfaces to be oriented arbitrarily within the final 3-D system.

Using the origami method, we fabricated a functional microscale supercapacitor, which is essentially a nanostructured 3-D device. The device consists of one electrode placed on a fixed substrate and the other on a folding membrane. Folding over the single membrane flap brings the two electrodes together to form one supercapacitor cell. In addition to demonstrating the feasibility of our process in building actual devices with arbitrarily oriented nanostructured surfaces, the microscale supercapacitor could potentially be used as an effective, integrated power source for standalone microsystems. A supercapacitor is a type of capacitor in which the energy is stored within an electrochemical double layer at the electrode/electrolyte interface. It derives its high specific capacitance mainly from the high surface area of its electrode material. Various forms of carbon, including carbon nanotubes, make excellent supercapacitor electrodes and are commonly used in full-sized, macroscale devices. The electrode material in our origami supercapacitors was composed of 99 wt% Super P carbon black and 1 wt% polyvinylidene fluoride binder in N-Methyl-2-pyrroldione.

A simplified origami process using SU-8 as the membrane material was developed and applied to the fabrication of supercapacitors. To further simplify the fabrication process, spontaneous folding methods discussed previously were not incorporated in these devices, and the flaps were simply folded over manually using a probe tip. The fabrication process, shown in Fig. 1, consists of first defining the wires, bond pads, electrode areas, and hinges by depositing and patterning a metal layer. In the supercapacitor samples tested, a 2 μm gold layer and a 30 nm chromium adhesion layer were thermally evaporated onto a bare silicon substrate and subsequently patterned. Following metal deposition, a 15 μm SU-8 layer was spun on and patterned to create SU-8 flaps with open centers to allow access to the gold electrode.

FIG. 1. (Color online) Process flow for the SU-8 supercapacitors. (a) Deposit and pattern gold layer. (b) Spin on and pattern the SU-8 layer. (c) Etch away underlying silicon to release the SU-8 membrane from the substrate. (d) Deposit carbon electrode material. (e) Deposit electrolyte. (f) Fold over membrane.
areas underneath. The SU-8 flaps were released from the substrate by isotropically etching away the underlying silicon with xenon difluoride gas. Using a probe tip, the carbon electrode material was then deposited on top of the electrode areas and allowed to air dry. A small amount of electrolyte was placed between the two layers, as shown in Fig. 2(b), and the flap was folded over with a probe tip to create the completed device shown in Fig. 2(d). The gold hinges proved to be very robust and almost never failed during the folding process. However, some of the hinges did break during the release process, as the SU-8 segments shrank and imposed excessive strain on the hinges. This problem was minimized by optimizing the SU-8 baking recipe to reduce lateral shrinkage.

The origami supercapacitors were tested through galvanostatic charge and discharge measurements, cyclic voltammetry, and ac impedance spectroscopy. A 1.5 M solution of H2SO4 served as the electrolyte, but since aqueous electrolytes have relatively low decomposition voltages, nonaqueous media are also being considered to allow higher operating voltages. Figure 3(a) shows an experimentally measured galvanostatic charge and discharge voltage profile for a supercapacitor with carbon electrodes obtained using a Solartron 1470 Battery Test Unit. The supercapacitor was charged and discharged at a constant current of 0.5 μA, and the capacitance is given by the equation

$$ C = \frac{I}{dV/dt}, $$

where $I$ is the charge/discharge current and $V$ is the voltage across the two electrodes. Using Eq. (1), the corresponding capacitance was calculated to be $\sim 1.0 \mu F$. To verify the increase in capacitance provided by the nanostructured carbon electrodes, identical supercapacitors with bare gold electrodes were tested and found to have capacitance values of $\sim 0.02 \mu F$, or about 50 times less than the values obtained in devices with carbon electrodes.

The voltammogram for a supercapacitor with carbon electrodes, shown in Fig. 3(b), was obtained using a Pine Biopotentiostat (Model AFCBP1) at a voltage scan rate of 50 mV/s. A voltage range of $-0.6$ to $0.6$ V, as measured between the two carbon electrodes, was used. The voltage was scanned at a constant sweep rate $s$, and the resulting current response $I_c$ was recorded. By setting $I = I_c$ and $dV/dt = s$, Eq. (1) can be used to calculate the capacitance. The corresponding capacitance was verified to be $\sim 1.0 \mu F$ for devices with carbon electrodes and $\sim 0.02 \mu F$ for devices without carbon electrodes. $I_c$ was approximately $0.05 \mu A$.

The ac impedance analysis was conducted using a Solartron 1260 Impedance Gain/Phase Analyzer over a frequency range of 0.1 Hz to 5 MHz at 10 mV. Twenty points per decade were collected going from high to low frequencies. Figure 4 shows the Nyquist and Bode plots for a supercapacitor with and without the highly porous carbon electrodes, respectively. Devices with carbon electrodes demonstrated the usual semicircle at high frequencies and exhibited almost purely capacitive behavior at low frequencies, indicated by the almost vertical line in the Nyquist plot. Conversely, devices without carbon electrodes also showed almost purely capacitive behavior at low frequencies, but clearly did not have a semicircular region at high frequencies. The absence

![Fig. 2](image_url)  
Fig. 2. (Color online) (a) Schematic drawings of the origami supercapacitor with a single SU-8 flap before and (b) after folding. The drawing is not to scale, and the bond pads are actually located much farther away from the main device. (c) SEM images of the supercapacitor with nanostructured carbon electrodes (inset) before and (d) after folding. Rectangular etch holes, shown in (c) and (d), help speed up the membrane release process.

![Fig. 3](image_url)  
Fig. 3. (a) Galvanostatic charge and discharge voltage profile of a supercapacitor with carbon electrodes recorded at 0.5 μA between 0 and 0.6 V. (b) Cyclic voltammogram for the same device taken at a scan rate of 50 mV/s. The indicated voltage range (−0.6 to 0.6 V) is between the working and counter electrodes.

![Fig. 4](image_url)  
Fig. 4. (a) Nyquist and Bode plots showing the results of impedance spectroscopy performed on an origami supercapacitor with (a) carbon electrodes and (b) gold electrodes.
of the semicircular region suggests that, in devices without carbon electrodes, prompt electrochemical responses occurred on the electrode surface. On the other hand, increased resistance at higher frequencies for devices with carbon electrodes, as indicated by the semicircle, may be attributed to the fact that the ions in the electrolyte must migrate into the highly porous carbon structure; therefore, energy stored in the pores may only be withdrawn at low frequencies or through dc techniques. The semicircle indicates that, at frequencies greater than ~0.1 MHz, capacitance is greatly influenced by frequency, and the device does not behave like an ideal capacitor. By observing the low-frequency regions in both Nyquist plots of Fig. 4 and using the equation

\[ |Z''| = \frac{1}{2\pi f C_{dl}}, \]

where \( Z'' \) is the imaginary component of the complex impedance, \( f \) is the frequency, and \( C_{dl} \) is the associated double-layer capacitance, corresponding capacitance values of ~1.0 \( \mu \)F and ~0.02 \( \mu \)F were obtained for devices with and without carbon electrodes, respectively. The results from impedance analysis confirmed those obtained through galvanostatic testing and cyclic voltammetry.

By approximating the mass of the carbon on each electrode, the double-layer capacitance of ~1.0 \( \mu \)F, acquired through three separate testing methods, yields a specific capacitance of approximately 15 F/g of carbon. Theoretically, the double-layer capacitance per area of carbon black in 1 M H\(_2\)SO\(_4\) is 8 \( \mu \)F cm\(^{-2}\), and the surface area of the carbon used in our device is around 62 m\(^2\)/g. This leads to an approximate theoretical specific capacitance of 5 F/g for supercapacitors when using 1 M H\(_2\)SO\(_4\) as the electrolyte. This figure is within an order of magnitude of the experimentally obtained value, and the difference is possibly justified, since a more concentrated electrolyte (1.5 M H\(_2\)SO\(_4\)) was used in our devices, and many parameters used in theoretical and experimental calculations, such as the surface area and mass of the carbon paint, were approximate.

In conclusion, we have shown that a working supercapacitor can be fabricated via the Nanostructured Origami\(^{TM}\) process. Because the origami method of fabrication is based on standard 2-D fabrication tools and techniques, a wide range of origami devices, including the origami supercapacitor, can be integrated with pre-existing micro- and nanosystems. In addition, the origami supercapacitor benefits greatly from the use of nanostructured surfaces and 3-D geometry, two main features of origami fabrication. The use of high-surface area carbon electrodes with nanoscale pores and particles resulted in a 50× increase in capacitance, whereas the ability to vertically stack the layers resulted in devices with an areal footprint of less than 1 mm\(^2\). Future devices will incorporate more complex nanochip architecture to further increase electrochemical performance of the supercapacitors.

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