GRAPHENE POWER PACK

An Honors Project Manuscript

Presented by

Jose Lasalle

Completion Date:
May 2016

Approved By:

_____
Name Of Committee Chair, Department

_____
Name Of Committee Member, Department

ABSTRACT

Title: **Graphene Power Pack**
Author: **Jose Lasalle**
Thesis/Project Type: **Independent Honors Project**
Approved By: **Ramakrishna Janaswamy, Electrical And Computer Engineering**
Approved By: **K.S. Yngvesson, Electrical And Computer Engineering**

The evolution of technology in mankind's recent history has been rapid and expansive. New disciplines emerge in this flourishing field of engineering, and at the core of every new venture or innovation is energy. One of the bottlenecks for discrete miniature and portable devices is on-chip energy storage, which requires a micro-scale battery or capacitor. On the opposite side of the energy spectrum, a lack of inexpensive and large-scale energy storage has limited the renewable energy industry, as many electricity-generating systems are tied to a grid that inefficiently handles the excess power and loses it in heat dissipation. An alternative to a mass overhaul of the power grid is a distributed network of high energy and high power storage banks. Another application is in electric vehicles, where the battery is currently the main limiting factor in practical functionality.

This project is an exploration of energy storage capabilities and power delivery of capacitors made from a material called graphene. This method is derived from that of the UCLA El-Kady group. The artifact of this project is a 12-element parallel integrated 535nF capacitor with a 13.6 nWh/cm^3 energy density. The benchmark is a source capable of producing 3V and 15mA to drive an LED for a 5 minutes (3.75 mWh) off of a flash charge. What was discovered in this project was the importance of an electrolyte for the devices. By using a mica-salt electrolyte paste, the capacitance of the devices increased by 5 orders of magnitude; however, that capacitance still did not stack up to the UCLA group's capacitance which was 4 orders of magnitude higher than that.

INTRODUCTION

The limitation of current technology rests in the drastic trade-off between power density and energy density (Figure 1). The characteristic devices representing high energy and high power are batteries and capacitors, respectively. Batteries store energy through electrochemical reactions. Capacitors store energy in an electric field between two conductors separated by a dielectric. A large amount of electrical energy can reside in batteries compared to capacitors, thus defining a high energy density for batteries and a low energy density for capacitors. However, the rate at which the battery charges and discharges that energy is fairly low compared to capacitors. Since power is equivalent to the rate of change of energy over a period of time, batteries are characterized as having low power density and capacitors, being devices that charge and discharge quickly, are characterized as having high power density.

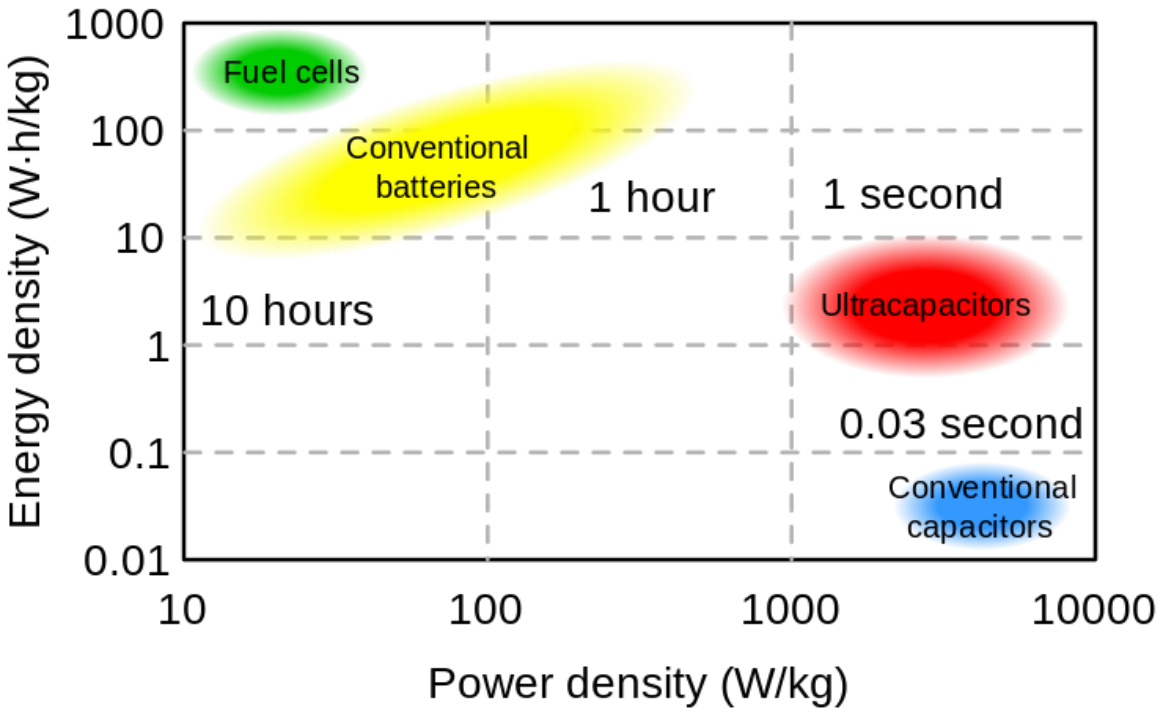


Figure 1. Ragone Plot shows the trade-off between power and energy density in various devices.

In recent years, groups from around the world have emerged with publications on advancements in solving this energy storage problem (see Appendix I for a literature review of this work). Of those groups, a subset has been working on a graphene and exploring its viability for high-grade energy storage. Of this subset, the El-Kady group of UCLA has done some of the most groundbreaking work.

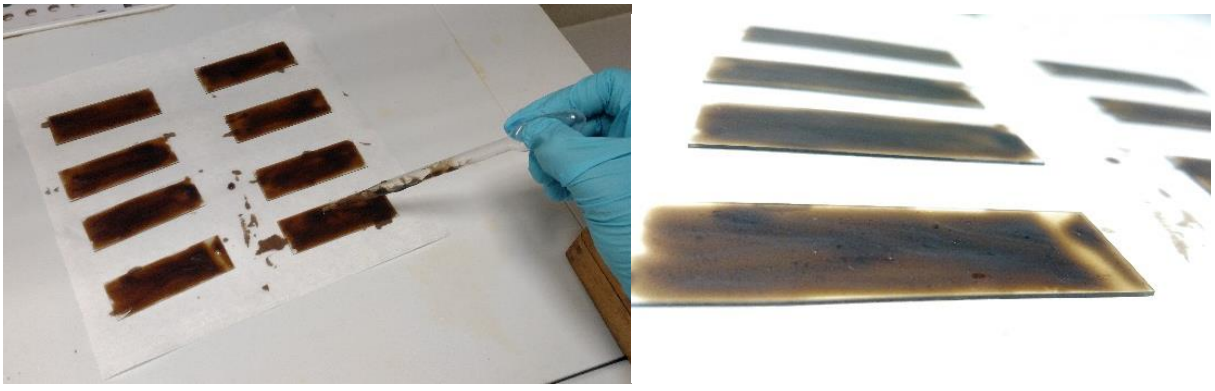
The hypothesis of this project was that if these samples, fabricated based on the work of the El-Kady group using the laser-scribed graphene method, prove to be comparable, one can develop an integrated device with higher energy density. Having utilized the materials and equipment provided by the electrical and computer systems engineering department here at UMass, as well as personal purchases using scholarships, I have made 36 samples for measurement. Using the

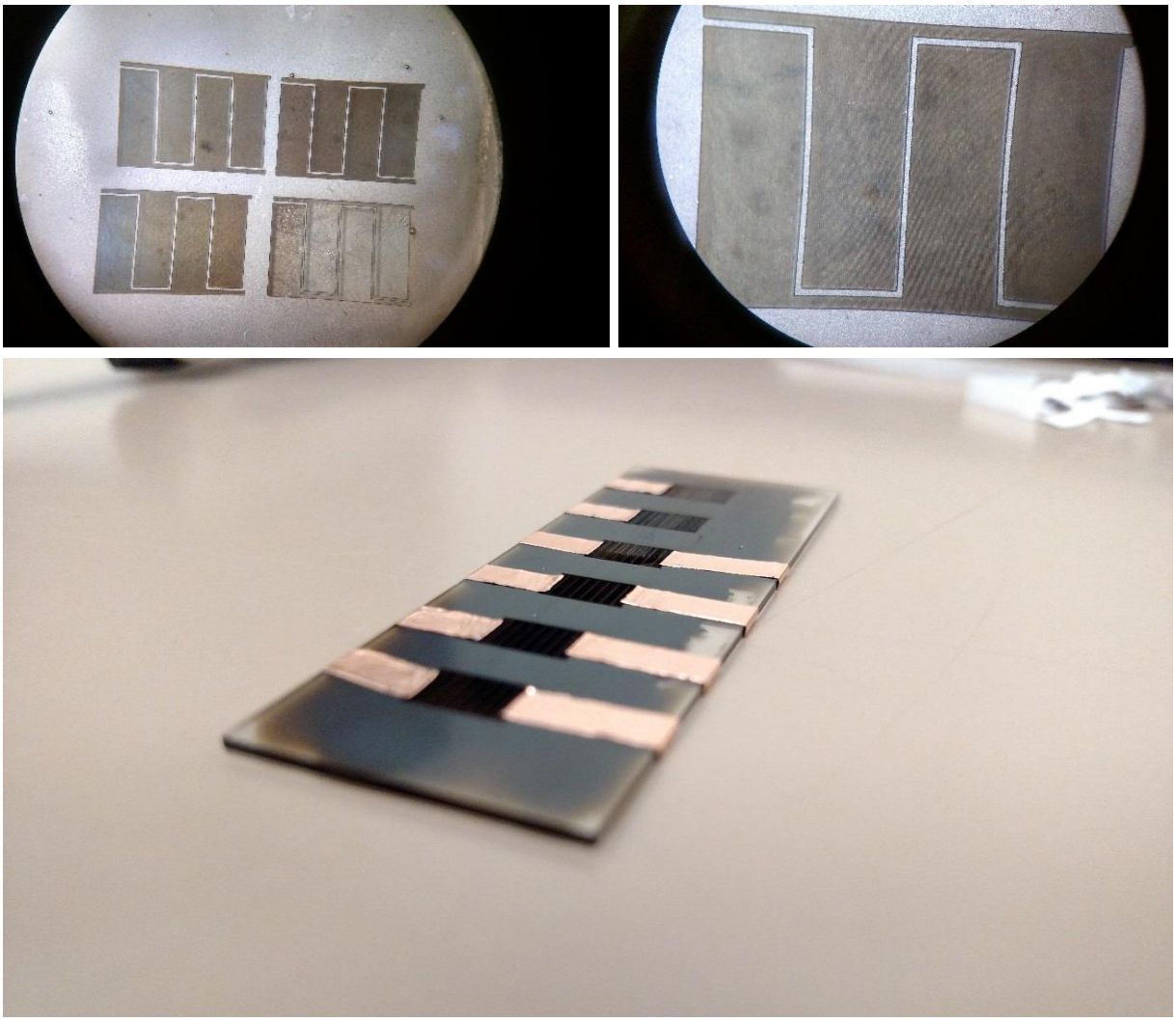
measurement equipment, as described in the METHOD section below, one is able to characterize the individual capacitors with regards to parameter such as capacitance, areal capacitance, volumetric stack capacitance, and energy density. Once characteristics for single devices are analyzed, single devices are capable of being configured into an integrated topology to optimize the characteristics of interest. In doing so, a 12-element parallel integrated 535nF capacitor with a 13.6 nWh/cm^3 energy density was created.

Regarding the electrolyte, the UCLA group and others use electrolyte gels in the capacitors as an essential component for high energy and power density. The electrolyte serves as a medium for ions to diffuse from one capacitor electrode to the other, allowing for a short mean ionic path that gives rise to a high power density. The electrolyte also has intrinsic salt ions, which intensify the electric field and increases the energy density. Given the fact that the gels developed by the other groups are chemically demanding to manufacture as well as caustic, the electrolyte for this project is a simple paste that can be made at home. The solid structure of the paste is a wet-ground mica. Mica is a silicate sheet composed of variations of combinations of potassium, sodium, calcium, aluminum, magnesium, iron, silicon and aluminum, which has a tendency towards stacked psuedohexagonal crystals that are maintained when wet-ground. Salt from the Dead Sea was then added to the paste to increase the amount of ions present for charging the capacitor. Additionally, the literature suggests that Graphene Oxide (GO) is a good ionic conductor, and therefore GO was also tested as an electrolyte.

METHODOLOGY & EXPERIMENTAL SECTION

Regarding graphene capacitor sample design, preparation, and fabrication, one will need graphene oxide (GO) solution (250mL), glass microscope slides and carry case (pack of 50), disposable pipettes (pack of 100), copper tape (1 reel), AutoCAD for layout design, and LPKF Protolaser U3 (355nm). For measurement, one will need an LRC meter, wires and alligator clips for probing. Gloves and goggles are used as a safety precaution. On a level lab bench, napkins are laid out, and a subset of the glass slides are placed on top. Using a pipette, GO solution is dispersed evenly onto the glass slides. This yields GO films. The films are allowed to dry for 24 hours under ambient conditions. These films are then affixed in the LPKF Protolaser U3 for laser treatment. The laser irradiation process results in the removal of oxygen species and the reestablishment of the sp^2 carbons. This results in a change of conductivity of the film from the insulating GO, with a typical resistance of >20MΩ/sq to high conductivity laser scribed graphene of around 1738 S/m. The electrode patterns are displayed below, and can be designed in any 2D or 3D CAD software. Copper tape is used as the electrode for each capacitor terminal, and alligator clips are used to provide easy connectivity.





The capacitance of each device is measured using the capacitance meter, which has an operating voltage window of 0.82V. Specific areal capacitance is calculated based on the area or volume of the device according to the following formulae:

$$\text{Areal Capacitance} = C_{device}/A$$
$$\text{Volumetric Stack Capacitance} = C_{device}/V$$

Where A and V refer to the area (0.4028 cm^2) and the volume (area*thickness = 0.4028 cm^2 * 7.6 um = 3.06e-4 cm^3) of the device, respectively. The energy density of the device is calculated from the formula:

$$E = C_V (\Delta E)^2/(2*3600)$$

Where E is the energy density (Wh/cm^3), C_V is the volumetric stack capacitance (F/cm^3) and ΔE is the operating voltage window (V). The factor of 3600 is a conversion from seconds to hours.

RESULTS AND DISCUSSION

The fabrication of these capacitors was successful. Below is a table of the capacitances and energy densities of the graphene capacitors with various electrolytes dispersed on top. S#.# denotes the sample, DSS denotes dead sea salt, and GO denotes graphene oxide.

Sample	*ΔE (V)*	*C (nF)*	*CA (nF/cm2)*	*CV (nF/cm3)*	*Energy (nWh/cm3)*
S6.3	0.82	0.015	0.0372393	48.9991115	0.004575973
S6.3-Mica	0.82	10	24.826216	32666.0743	3.050648385
S6.3-Mica-DSS	0.82	700	1737.8352	2286625.2	213.545387
S6.1	0.82	0.03	0.0744786	97.998223	0.009151945
S6.1-GO	0.82	10	24.826216	32666.0743	3.050648385
S6.1-GO-DSS	0.82	200	496.52433	653321.486	61.01296771
Mica	0.82	12.5	31.032771	40832.5929	3.813310482
Mica-DSS	0.82	200	496.52433	653321.486	61.01296771
S4&5-Parallel	0.82	535	110.68355	145636.248	13.60080738
UCLA	2.5	5E+09	1.191E+10	1566720000	1360000

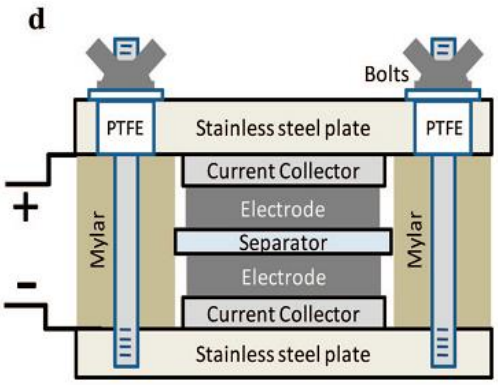
The capacitance tends to be in the low tens of pF, which greatly increases with electrolytes. Adding mica raised the capacitance by around 1000, GO by 1000, and salt by an additional 200-700 times the original value. Even with these results, the energy density is 4 orders of magnitude less than UCLA's capacitors that are capable of driving an LED. For *S4&5-Parallel*, both glass slides were sandwiched with mica and dead sea salt in between and the leads were connected in parallel. This capacitance is significantly smaller than a theoretical 12-element parallel connection of S6.3-Mica-DSS which would be 8.4uF. However, this smaller capacitance can be attributed to the decrease in the amount of mica-salt paste that lies over the graphene capacitors, therefore reducing the amount of ions available for energy transport and electric field density. This exemplifies the trade-off between low-profile form factor devices and energy density. Additionally, these findings demonstrate a large dependence on the electrolyte. Given that I did not have the skills to replicate the electrolyte gels used in other research group capacitors, it is understandable that these devices are outperformed by ones produced by UCLA.

CONCLUSION

The main outcomes of this project are that small scale graphene capacitors can be fabricated with resources typically available at research universities and that the energy density greatly depends on the electrolyte. Because of the ease of fabrication, disregarding the electrolyte, I was able to make a large number of samples for experimentation. Nevertheless, due to a suboptimal electrolyte, none of these devices were able to light an LED as the UCLA group had. Though this benchmark was not met, this project leaves room for further improvement. For example, the primary step in optimizing these devices is to develop an electrolyte gel that maintains a high ionic conductivity and low mean ionic path for fast energy transport of a large amount of ions. There is great need for equivalent series resistance and power density measurements to determine how quickly these devices can charge and discharge, as well as characterize their efficiency. With future work ahead, this project still succeeded in fabricating graphene capacitors and characterizing them with regard to capacitance and energy density.

APPENDIX 1: LITERATURE REVIEW

INTRODUCTION



The growing technological demands of humanity have motived the electric power industry to innovate energy storage devices optimized for high and sustained energy and power density. Such emerging sectors as portable electronic devices, miniature electronics, distribution, and renewable energy contribute to this demand for platforms from on-chip energy storage to home battery systems. Tesla PowerWall has made great strides in this field regarding high energy storage, on the order of 10kWh; however, this lends itself to a degree of limitation when taking into consideration the needs of the low-energy device industries. Microscale supercapacitors have great potential to complement or replace batteries and electrolytic capacitors (ECs) in various applications. Batteries and ECs stand at opposite ends of the spectrum in terms of their power and energy densities. Batteries store energy through electrochemical reactions and can exhibit high energy densities (20-150 Wh/kg), whereas ECs, which store charge in electrochemical double layers (EDLs), can only achieve values of 4-5Wh/kg [2]. However, ECs can deliver higher power densities than batteries as ion flow is faster than redox reactions. ECs are also generally maintenance free and display a longer shelf and cycle life, so they are often favored in many electronic applications. An EC that combines the power performance of capacitors with the high energy density of batteries would represent a major advance in energy storage technology, but this requires an electrode with higher and more accessible surface area than that of conventional EC electrodes while maintaining high conductivity. Graphene-based materials are promising micro-electrochemical energy storage devices because of their mechanical and electrical properties as well as exceptionally high surface area. Additionally, the individual graphene capacitor cells have proven to provide scalable power and energy density by configuring multiple cells in certain topologies. This review surveys the latest advances in graphene-based planar interdigital ECs, from the history of graphene materials manufactured for capacitor use, fabrication techniques, electrolyte materials, and device configurations for scalable power. Finally, developmental directions of future graphene-based micro-supercapacitors for broad spectrum energy storage applications are discussed.

SUPERCAPACITORS

The typical design for a supercapacitor is a stacked configuration of current collectors, electrodes, an electrolyte medium, and a separator in the middle (Figure to right) [7]. The electrolyte is mainly comprised of a conductive liquid mixture of an aqueous or organic solvent that can diffuse into the electrodes during the charging process and diffuse out of the electrode during discharge. Separating the two electrodes is an ion-permeable membrane that serves as a separator to prevent a short circuit. The current collectors, being metallic and highly conductive, electrically connect the electrodes to an external circuit [4]. The performance of supercapacitors depends on the properties of their active materials, fabrication of electrodes, selection of electrolytes and geometry of the devices.

GRAPHENE SUPERCAPACITORS

Due to its distinctive structure and properties, graphene has invoked great interest in a wide range of scientific fields ranging from condensed matter physics to materials science. Graphene has the potential to contribute to studies and applications of electronics, polymer hybrids, transparent conducting electrodes, batteries and supercapacitors [9]. The possibilities of this material also extend to sensors, dye-sensitized solar cells, field emission, catalysts, and more. Due to its high conductivity, significant surface area (∼2630 m2g−1), exceptional intrinsic double-layer capacitance (∼21μFcm−2) and high theoretical capacitance (∼550Fg−1), graphene-based materials have been demonstrated as one class of the most promising and attractive electrode materials for supercapacitors [2, 1]. Additionally, graphene-based thin films hold great promise for developing new types of flexible, transparent and miniaturized ultrathin supercapacitors, known as microsupercapacitors (MSCs). In configurations that allow for electrolyte ions to easily interact with all layers of graphene in the horizontal direction are superior to conventional devices [3, 12]. Such devices are classified as planar microsupercapacitors.

HISTORY OF PLANAR INTERDIGITAL MSCS

As industry and research continues to develop ultrathin and flexible electronics, planar MSCs have attracted great attraction. Contrasting with the traditional stack geometry of supercapacitors, planar MSCs are unique in that they allow for much thinner devices, smaller devices, and more flexible devices on an arbitrary substrate. These characteristics allow for electrolyte ions to migrate between the narrow interspaces between the electrode fingers, thus decreasing the ion diffusion distance and offering an ultrahigh power capability [1]. This planar configuration does not call for the separator that is used in most conventional supercapacitors with a stack geometry. Also, this configuration creates many opportunities for large-scale fabrication of small devices on a substrate in a practically two-dimensional horizontal plane for direct integration with electronics [1]. Modern stack geometry is not favorable for the transport of ions in electrolytes, causing great power losses. In addition to power loss, conventional supercapacitors face challenges regarding integration into electronics because of the intensive manufacturing processes for building the stacked layers with electrolytes and external connections [6]. For these reasons, planar MSCs have value for their ease in manufacturing electronically isolated electrodes in the same plane. Additional merit is derived from the MSC's broad suitability for numerous electrolytes, the easy adjustment of electrode patterns, and low internal impedance due to the short distance between interdigital electrodes.

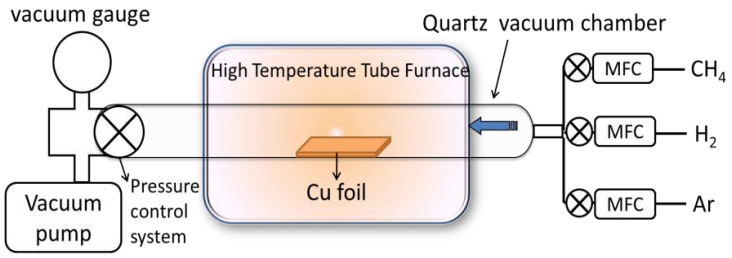
The first reported prototype of planar MSCs with a liquid electrolyte on a silicon substrate was by Sung et al. in 2003. Subsequently, he and his group made great contributions to the design and fabrication of all-solid state and flexible MSCs [8]. Since then, a subset of the scientific community has directed its attention to the development of planar MSCs by focusing on the fabrication of original nanostructured electrode materials. Such interest in thin-film devices has lead to numerous techniques for development, such as electrochemical polymerization, inkjet printing and layer-by-layer assembly, as well as the formation of new device structures from 2D to 3D microelectrodes [9]. The main objective of these developers and their techniques is to improve the energy and power densities as well as the cycling lifetime and frequency response of the MSCs. Many MSCs have been made since, and have exhibited promising volumetric stack capacitance. However, most suffer from low charge and discharge efficiency, frequency response

and power capability. Exceptionally, carbon-based MSCs show a competitive and attractive potential for achieving high-frequency response and rate capability.

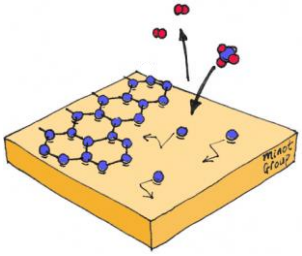
METHODS OF PRODUCTION

Graphene for MSCs can be prepared by both bottom-up (such as chemical vapor deposition, arc-discharge, unzipping carbon nanotubes, and epitaxial growth on SiC) and top-down approaches (thermal, chemical, and photo reduction of exfoliated graphite derivatives, such as graphene oxide). The methods herein discussed are chemical vapor deposition (CVD) and reduction.

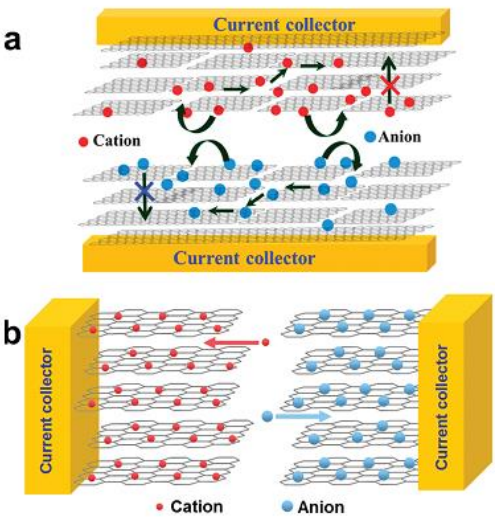
BOTTOM-UP APPROACH: CVD



Chemical vapor deposition (CVD) is a chemical process used to produce high quality, high-performance, solid materials. The process is often used in the semiconductor industry to produce thin films with molecular accuracy. In typical CVD, the wafer (substrate) is placed in a high temperature, low-vacuum tube furnace and is exposed to one or more volatile precursors of graphene, which in most cases is carbon containing methane gas. These precursors react and decompose on the substrate surface to produce the desired deposit of graphene, as illustrated in the figure to the right. Frequently, volatile by-products are also produced, 2H2 in the case of methane, which are removed by gas flow through the reaction chamber.

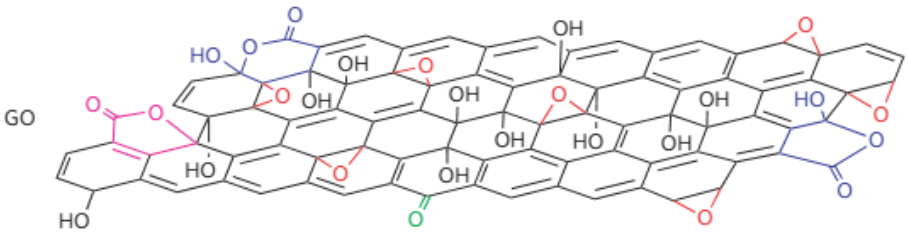


Yoo et al. reported fabrication of ultrathin planar supercapacitors based on graphene. One method involved the use of CVD-grown monolayer graphene in perpendicular orientation to the current collectors [11]. This architecture presents the added benefit of increased ability of the electrolyte to percolate into the layers of graphene to allow for the full utilization of the electrochemical surface area (Figure to left). As mentioned previously, planar MSCs are favorable for electrolyte ions to interact with the whole surface of the graphene sheets in a short ion diffusion distance [11].



TOP-DOWN APPROACH:

Among the methods of fabrication, the top-down approach, starting from graphene oxide, is claimed to be the most promising method for potential uses in polymer composites for MSCs. There are two important reasons supporting this claim. First, graphene oxide is readily dispersible in water and easily modified to be dispersed in both polar and non-polar polymer matrices. Secondly, graphite had a global production of more than 1.1 million tons and a cost of $825 per ton in 2008 [13].



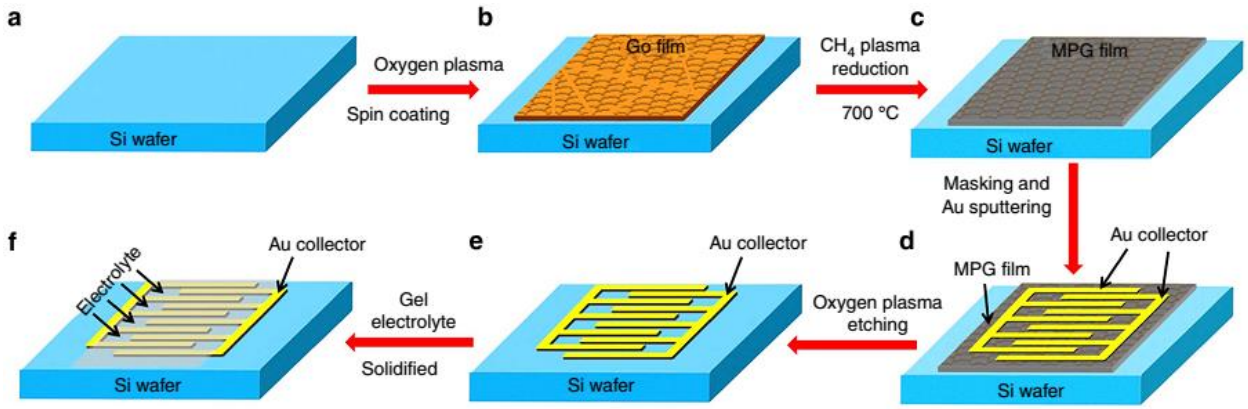
These express the abundance and affordability of this versatile material.
As illustrated in the figure above, graphene oxide is oxidized graphene, where the previously free electrons bond with oxygen groups [3]. Reduction refers to the loss of oxygen deficiencies in the graphene lattice, resulting in a layer or few layers of graphene. GO is a centerpiece of many top-down approaches. As mentioned before, the top-down approaches to be mentioned are methane plasma reduction, and photo reduction.

TOP-DOWN APPROACH: METHANE PLASMA REDUCTION

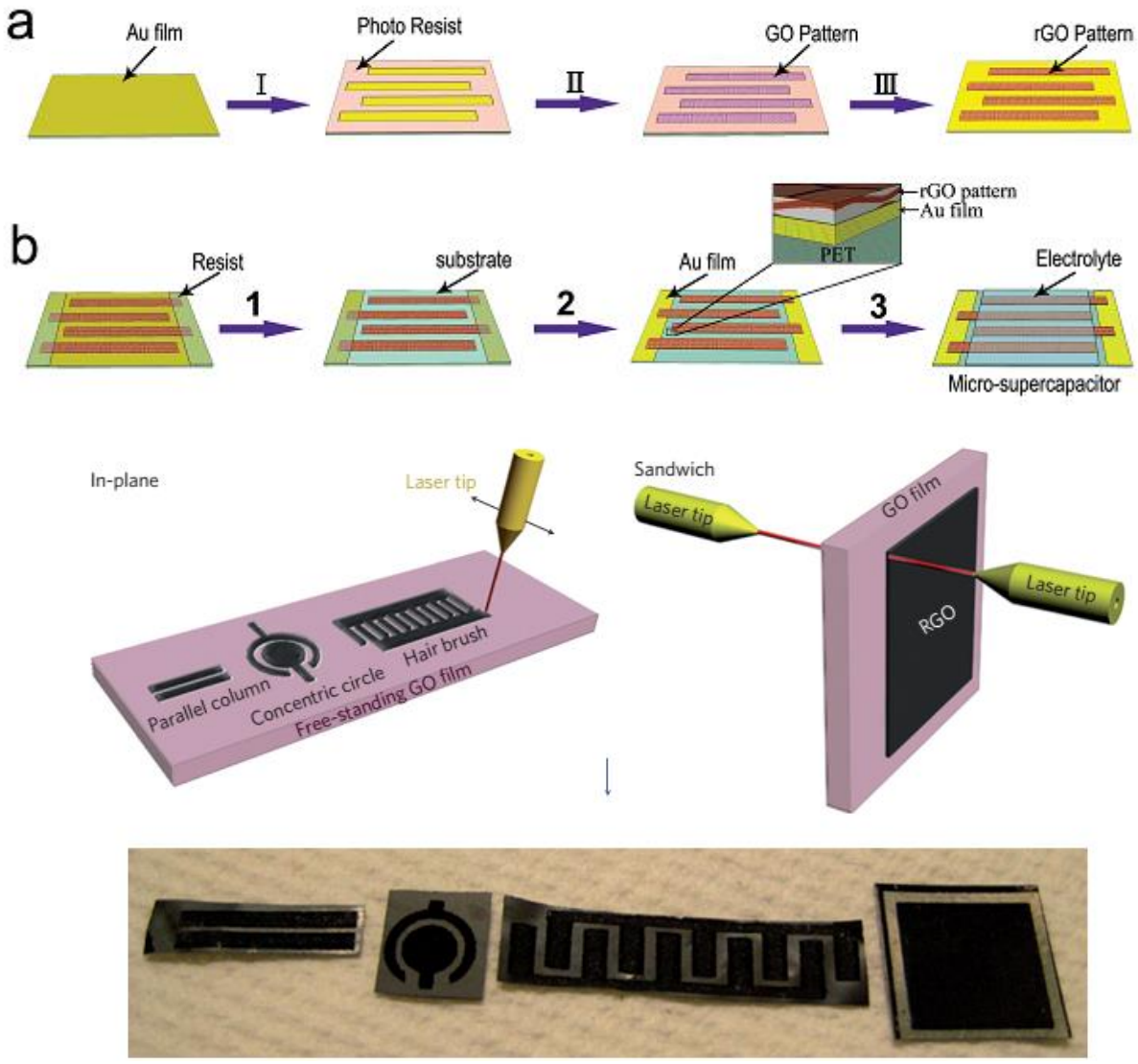
Although the performance of the graphene-based MSCs has been significantly improved by developing thin-film manufacturing technologies and device architectures, their power densities remain far from those of electrolytic capacitors and their energy densities are much lower than those of lithium thin-film batteries. Recently, Wu et al. demonstrated a novel class of graphene-based planar interdigital MSCs based on methane plasma reduced graphene films (denoted MPG) micropatterned on arbitrary substrates, both rigid and flexible [10]. The figure below illustrates the fabrication process of the micro-supercapacitors on a silicon wafer. First, a thin film of graphene oxide (GO) was obtained by spin-coating a GO dispersion on a modified silicon wafer that was first treated with oxygen plasma. Next, the GO film was rapidly reduced by methane (CH4)–plasma treatment at 700C over a short time (20 s), as indicated by the color change of the film from yellow to grey. When the process is complete, what results is an all solid-state MPG-based MSC with an in-plane geometry.

TOP-DOWN APPROACH: PHOTO REDUCTION

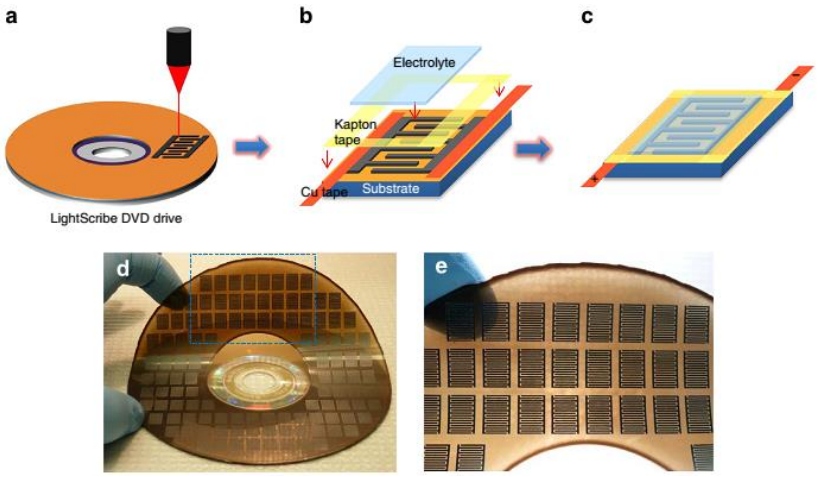
Photo reduction is a photothermal process by which the light from a light-source serves to heat the surface of the graphene oxide, where the graphene oxide reduces to graphene at around 200C. Physically, the lattice oscillations mutually arise with the heating of the lattice and the energy of these vibrations surpass that of the bond-dissociation energy between the carbon atoms and the carboxylate groups. This results in the removal of the carboxylate and other oxygen group defects from the GO film. What remains is single to few layer graphene sheets.
Recently, Niu's group developed flexible, ultrathin and all-solid-state graphene-based MSCs, using H3PO4/PVA gel electrolyte, through the combination of photolithography with electrophoretic deposition to produce ultrathin rGO interdigital electrodes on a polyethylene terephthalate (PET) substrate [5]. Below is a schematic illustrating the process of preparing rGO



micro-supercapacitors directly on a substrate by combining photolithography with electrophoresis. The first procedure, a, is patterning the surface of Au film with resist in the form of the desired device structures by photolithography and fabricating rGO electrode patterns with microscale gaps using electrophoretic buildup. The process goes as such: I) patterning and exposing the surface of Au film with resist in the form of the desired interdigited structures; II) constructing GO interdigited structures by electrophoretic deposition; and III) reducing GO to rGO. The second procedure, b, is fabricating all-solid-state micro-supercapacitors using rGO patterns as electrodes. This process goes as such: 1) protecting the Au film on both end of rGO interdigited structures by resist and etching the Au film which is not coated by rGO pattern; 2) removing the resist that coat on both end of rGO interdigited structures; and 3) coating H 3PO 4/PVA electrolyte.



To explore the potential of planar supercapacitors, Gao's group developed all-graphene based MSCs by direct laser reduction and patterning of hydrated graphite oxide (GO) films [3]. It was found that the water trapped in GO enables it to act as a good ionic conductor and electrical insulator between the two rGO electrodes. For this reason, the GO serves as an electrolyte and an



electrode separator with ion transport characteristics. On a piece of GO paper, both planar and conventional stacked-geometric supercapacitor designs were directly constructed in a number of patterns and shapes to test the superiority of the devices (Figure above). Laser reduction was conducted with a CO2 laser printer (Universal X-660 Laser Cutter Platform; power, 2.4 W; scanning speed, 30%). The ability to laser reduce GO into conducting reduced graphite oxide (RGO) allows the facile and non-toxic writing of RGO–GO–RGO patterns in various configurations to build electrical double-layer capacitors (EDLC) or supercapacitors.

Considering the fact that the conventional microfabrication methods involving lithographic techniques or using masks for making micropatterns on substrates are cumbersome for fabricating lowcost micro-devices for widespread applications, El-Kady and Kaner recently reported a scalable fabrication method for graphene-based planar MSCs by direct laser writing on GO films using a standard LightScribe DVD burner [1]. This technique is a simple, low-cost high-throughput lithographic technique that does not require masks, additional processing or complex operations. The figure on the next page shows the fabrication of laser-scribed graphene MSCs (LSGMSCs). First, a disc with a GO film is inserted into a LightScribe DVD drive, and a computer-designed circuit is written to produce graphene pattern on the GO film by a laser. Second, a copper tape is glued along the edges of the electrodes to improve electrical contact, and the whole interdigital area is covered by a polyimide tape. Finally, an electrolyte is added to obtain a planar LSG-MSC. This process is readily scalable for the efficient fabrication of solid micro-devices that are thin (~7.6μm) and flexible. For instance, more than 100 microdevices can be quickly produced on a flexible substrate in 30 min or less.

EXPERIMENTAL FINDINGS

The important characteristics of supercapacitors are the specific/intrinsic capacitance [μFcm−2 , or Fg-1], stack/volumetric capacitance [Fcm-3], power density [W cm-3], energy density [mWh cm-3], conductivity [Scm-1], internal resistance [ohms], time-constant [s], specific surface area [m2/g] and cycling stability [%capacitance retention after a number of cycles at a voltage scan rate of Vs-1]. Though not every group reported the same parameters, there are still meaningful comparisons presented. The resulting planar supercapacitors produced by Yoo's group via CVD showed a dramatic increase in capacitance compared to conventional stacked-geometry supercapacitors. The novel ultrathin planar devices delivered a specific capacitance of~80μFcm−2. Similarly, the MPG-based MSCs with the H2SO4/PVA gel electrolyte created by Wu's group deliver a capacitance of~80.7μFcm−2, a stack capacitance of~17.9 F cm−3, a power density of 495 W cm−3 (higher than that of electrolytic capacitors) and an energy density of 2.5 mWh cm−3 that is comparable to lithium thin-film batteries, in association with superior cycling stability (~98.3% capacitance retention after 100 000 cycles at an ultrahigh scan rate of

50Vs−1). Also due to the high electrical conductivity (~345 S cm−1) of the MPG films and the planar geometry, these microdevices allow operation at ultrahigh rates up to 1000Vs−1, three orders of magnitude higher than conventional supercapacitors, highlighting the superiority of the planar device geometry over the classical sandwichlike stack geometry for supercapacitors. The fabricated MSCs can also work collaboratively when connected in parallel or in series to meet certain applications that require higher operating currents and voltages in a short time. Furthermore, the devices show an extremely small time constant of~0.28 ms that allows them to work in progressively ultrafast charge and discharge conditions [10].
Because of the short ion diffusion pathway, the resulting rGO-MSCs created by Niu's group exhibited a specific capacitance of 286 F g−1, three times higher than that of conventional rGO-based supercapacitors (~86 F g−1). Significantly, the MSCs can be interconnected in series on one chip to improve the output potential, suggesting the promise for applications in integrated electronics. Gao's group found that the planar supercapacitor with a concentric circular geometry delivered a capacitance of ~0.51 mF cm−2, which turned out to be nearly twice that of the sandwich supercapacitor. Additionally, the circular MSC demonstrated good cyclic stability, dropping around 35% in capacitance after 10000 cycles. By introducing external electrolytes, such as aqueous electrolyte (1.0 M Na2SO4) and an organic electrolyte (1.0 M TEABF4), the capacitance and energy density of the planar devices were improved. The drawbacks of this method include poor frequency response, large internal resistance (6.5kΩ), and low rate capability, possibly caused by a long distance between the planar electrodes. Nevertheless, the trade-offs still make this method of production promising for large scale production. The MSCs constructed by El-Kady et al. could be built with a hydrogel-polymer electrolyte (H2SO4/PVA) or an ionogel electrolyte (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with fumed silica) that respectively allow the operation of the device at a voltage window of 1 V or 2.5 V. The LSG-MSCs have improved charge-storage capacity and rate capability, and offer a resistor–capacitor time constant of 19 ms, a power density of ~200 Wcm−3, a volumetric capacitance of 3.05 Fcm-3, an areal capacitance of 2.32 mFcm-2, a surface area of 2630 m2g-1, and >90% cycling stability for flexibility and charge/discharge cycles.

CONCLUSION

Presented was a comparison of development techniques of graphene-based materials for on-chip planar interdigital MSCs, which combine the advantages of both graphene and a planar geometry. In particular, the 2D ultrathin structure, excellent electrical conductivity, high surface area (~2630 m2g−1) and high theoretical capacitance (~550 Fg−1) of graphene enable it to be a very promising electrode material for planar MSCs that can greatly improve the charge and discharge performance, promote the rapid diffusion of ions into or out of the internal structure of the electrodes using short pathways, and increase the accessibility of ions to the surface of all the parallel graphene sheets on substrates [11]. Furthermore, the planar device geometry provides two major merits compared with conventional supercapacitor devices with a stacking geometry of thin-film electrodes. One is that both positive and negative electrodes are in one plane, which allows for elaborate integration with an electronic device chip [1]. Another advantage is the improved performance of planar MSCs with interdigital electrodes compared to that of conventional devices [10]. As a result, the latest advancements of graphene-based interdigital MSCs have demonstrated outstanding electrochemical performance with a large scan rate, fast frequency response, long-term cycling stability, and ultrahigh power and energy densities, which

are superior to the classical sandwich-type supercapacitors and any other previously reported MSCs with other carbons as electrode materials [1, 11].

The research and development of graphene-based MSCs are still in early stages and many issues remain to be solved. To further development of graphene-based MSCs, researchers are considering the integration of the following aspects into one device. The first potential area of development is the designed fabrication of nanostructured electrode materials [9]. The ability to tune the morphology and microstructure of graphene sheets on films is a very important feature to increase the performance of the resulting MSCs. Understanding the complex relationship between the structure and capacitive performance of graphene materials is absolutely necessary to improve the design of high-performance graphene-based MSCs.

The next challenge for developing high performance MSCs is to produce large-area, uniform, conductive films on any substrate of choice. To address this challenge, one ought to consider the material's compatibility with the substrate and the scalability of thin-film techniques for efficient production of continuous large-area thin films. Some commonly used techniques for meeting these goals include inkjet printing and screen printing. These techniques are inexpensive, rapid and capable of mass production for the large-scale fabrication of thin-film-based MSCs on a broad variety of substrates, such as silicon wafers, paper, plastics, etc. However, there has yet to be a systematic study of their use for producing graphene-based materials for MSCs. It is expected that these techniques should be both useful and readily applicable to the thinfilm processing of a wide range of materials for large area devices which can be easily incorporated into electronics.

A third point of optimization of device architectures is addressing the challenges of energy and power densities. This aspect involves a study of geometric parameters such as the interspace between electrodes, width, length, and number of interdigital fingers. The active area is directly proportional to the energy storage capabilities, and can be increased by widening and elongating the fingers. This would decrease the resistance and therefore increase energy and power densities of the devices. Additionally, developing three-dimensional graphene-based interdigital MSCs by lithographical microfabrication techniques can increase the amount of active material per area while fast ion diffusion is unaffected, leading to an improvement of the output power and energy [9]. Practically, the connection of two or more MSCs in parallel and/or series within one MSC pack on a large area substrate is expected to be a promising strategy to meet the requirements for portable electronics, other on-chip uses and large-scale energy storage [10]. This marks my area of interest, as I aim to explore the feasibility of high energy storage and power delivery by large arrays of graphene MSC cells.

Further improvement in the performance of graphene-based MSCs can be achieved through the optimization of parameters such as the electrode material, the electrolyte, the nanostructure design, and the fabrication techniques. By this review, it is evident that the need for micro-scale energy storage can potentially be filled by graphene-based MSCs, as they promise uniquely high micro-electrochemical energy-storage that can provide enough power to satisfy the requirements for a great number of applications in miniaturized electronic devices. Expanding on this, my project will begin at the point where the El-Kady group left off in combining multiple devices for high power and energy capacitors [1].

REFERENCES

1. El-Kady, Maher F., and Richard B. Kaner. 2013. Scalable fabrication of high-power graphene micro-supercapacitors for flexible and on-chip energy storage. *Nature Communications* 4 : 1475.

2. El-Kady, M. F., V. Strong, S. Dubin, and R. B. Kaner. 2012. Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. *Science (New York, N.Y.)* 335 (6074) (Mar 16): 1326-30.

3. Gao, Wei, Neelam Singh, Li Song, Zheng Liu, Arava Leela Mohana Reddy, Lijie Ci, Robert Vajtai, Qing Zhang, Bingqing Wei, and Pulickel M. Ajayan. 2011. Direct laser writing of micro-supercapacitors on hydrated graphite oxide films. *Nature Nanotechnology* 6 (8): 496-500.

4. Kötz, R., and M. Carlen. 2000. Principles and applications of electrochemical capacitors. *Electrochimica Acta* 45 (15): 2483-98.

5. Niu, Zhiqiang, Li Zhang, Lili Liu, Bowen Zhu, Haibo Dong, and Xiaodong Chen. 2013. All-Solid-State flexible ultrathin Micro-Supercapacitors based on graphene. *Advanced Materials* 25 (29): 4035-42.

6. Pech, David, Magali Brunet, Ty Mai Dinh, Kevin Armstrong, Julie Gaudet, and Daniel Guay. 2013. Influence of the configuration in planar interdigitated electrochemical micro-capacitors. *Journal of Power Sources* 230 : 230-5.

7. Stoller, Meryl D., Sungjin Park, Yanwu Zhu, Jinho An, and Rodney S. Ruoff. 2008. Graphene-based ultracapacitors. *Nano Letters* 8 (10): 3498-502.

8. Sung, Joo-Hwan, Se-Joon Kim, and Kun-Hong Lee. 2003. Fabrication of microcapacitors using conducting polymer microelectrodes. *Journal of Power Sources* 124 (1): 343-50.

9. Wu, Zhong-Shuai, Xinliang Feng, and Hui-Ming Cheng. 2013. Recent advances in graphene-based planar micro-supercapacitors for on-chip energy storage. *National Science Review*: nwt003.

10. Wu, Zhong–Shuai, Khaled Parvez, Xinliang Feng, and Klaus Müllen. 2013. Graphene-based in-plane micro-supercapacitors with high power and energy densities. *Nature Communications* 4 .

11. Yoo, Jung Joon, Kaushik Balakrishnan, Jingsong Huang, Vincent Meunier, Bobby G. Sumpter, Anchal Srivastava, Michelle Conway, Arava Leela Mohana Reddy, Jin Yu, and Robert Vajtai. 2011. Ultrathin planar graphene supercapacitors. *Nano Letters* 11 (4): 1423-7.

12. Luong, Nguyen Dang, Nikolaos Pahimanolis, Ulla Hippi, Juuso T. Korhonen, Janne Ruokolainen, Leena-Sisko Johansson, Jae-Do Nam, and Jukka Seppälä. 2011. Graphene/cellulose nanocomposite paper with high electrical and mechanical performances. *Journal of Materials Chemistry* 21 (36): 13991-8.