Engineering three-dimensional hybrid supercapacitors and microsupercapacitors for high-performance integrated energy storage

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Supercapacitors now play an important role in the progress of hybrid and electric vehicles, consumer electronics, and military and space applications. There is a growing demand in developing hybrid supercapacitor systems to overcome the energy density limitations of the current generation of carbon-based supercapacitors. Here, we demonstrate 3D high-performance hybrid supercapacitors and microsupercapacitors based on graphene and MnO_2 by rationally designing the electrode microstructure and combining active materials with electrolytes that operate at high voltages. This results in hybrid electrodes with ultrahigh volumetric capacitance of over 1,100 F/cm^3. This corresponds to a specific capacitance of the constituent MnO_2 of 1,145 F/g, which is close to the theoretical value of 1,380 F/g. The energy density of the full device varies between 22 and 42 Wh/l depending on the device configuration, which is superior to those of commercially available double-layer supercapacitors, pseudocapacitors, lithium-ion capacitors, and hybrid supercapacitors tested under the same conditions and is comparable to that of lead acid batteries. These hybrid supercapacitors use aqueous electrolytes and are assembled in air without the need for expensive "dry rooms" required for building today's supercapacitors. Furthermore, we demonstrate a simple technique for the fabrication of supercapacitor arrays for high-voltage applications. These arrays can be integrated with solar cells for efficient energy harvesting and storage systems.

supercapacitor | microsupercapacitor | graphene | metal oxide

As a result of the rapidly growing energy needs of modern life, the development of high-performance energy storage devices has gained significant attention. Supercapacitors are promising energy storage devices with properties intermediate between those of batteries and traditional capacitors, but they are being improved more rapidly than either (1). Over the past couple of decades, supercapacitors have become key components of everyday products by replacing batteries and capacitors in an increasing number of applications. Their high power density and excellent low-temperature performance have made them the technology of choice for backup power, cold starting, flash cameras, regenerative braking, and hybrid electric vehicles (2, 3). The future growth of this technology depends on further improvements in energy density, power density, calendar and cycle life, and production cost.

According to their charge storage mechanism, supercapacitors are classified as either electric double-layer capacitors (EDLCs) or pseudocapacitors (2). In EDLCs, charge is stored through rapid adsorption–desorption of electrolyte ions on high-surface-area carbon materials, whereas pseudocapacitors store charge via fast and reversible Faradaic reactions near the surface of metal oxides or conducting polymers. The majority of supercapacitors currently available in the market are symmetric EDLCs featuring activated carbon electrodes and organic electrolytes that provide cell voltages as high as 2.7 V. Although these EDLCs exhibit high power density and excellent cycle life, they suffer from low energy density because of the limited capacitance of carbon-based electrodes. The specific pseudocapacitance of Faradaic electrodes (typically 300–1,000 F/g) exceeds that of carbon-based EDLCs; however, their performance tends to degrade quickly upon cycling.

Studies during the past few years have demonstrated an attractive alternative to conventional EDLCs and pseudocapacitors by using hybrid systems. Using both Faradaic and non-Faradaic processes to store charge, hybrid capacitors can achieve energy and power densities greater than EDLCs without sacrificing the cycling stability and affordability that have so far limited the success of pseudocapacitors (4). Several combinations of materials, such as RuO_2 (5), Co_3O_4 (6), NiO (7), V_2O_5 (8), $Ni(OH)_2$ (9), and MnO_2 (10), have been studied for preparing hybrid supercapacitors. Among these, MnO_2-based systems are particularly attractive as MnO_2 is an earth-abundant and environmentally friendly material with a high theoretical specific capacitance of 1,380 F/g (11). However, the poor ionic (10^{-13} S/cm) and electronic (10^{-5}–10^{-6} S/cm) conductivity of pristine MnO_2 often limits its electrochemical performance. Recent reports show that some high-performance results can be achieved only from ultrathin MnO_2 films that are a few tens of nanometers in thickness (12). Nevertheless, the thickness and the area-normalized capacitance of these electrodes are not adequate for most applications. A promising approach to realize practical applications of MnO_2 is to incorporate nanostructured MnO_2 on highly conductive support materials with high surface areas such as nickel nanocones (13), Mn nanotubes (14), activated carbon (15), carbon fabric (16), conducting polymers (17), carbon nanotubes (18, 19), and graphene (20–24). Although promising

Significance

Batteries run just about everything portable in our lives such as smartphones, tablets, computers, etc. Although we have become accustomed to the rapid improvement of portable electronics, the slow development of batteries is holding back technological progress. Thus, it is imperative to develop new energy storage devices that are compact, reliable, and energy dense, charge quickly, and possess both long cycle life and calendar life. Here, we developed hybrid supercapacitors that can store as much charge as a lead acid battery, yet they can be recharged in seconds compared with hours for conventional batteries.

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Fig. 1. Rational design of high-energy–high-power hybrid supercapacitor electrodes. Improving the ionic current (IC) and electronic current (EC) within the electrode is a key. Different approaches have been explored including (*A*) compact thick films of metal oxide (here, MnO_2); (*B*) nanostructured metal oxide films; (*C*) addition of conductive materials to the nanostructured metal oxide; and (*D*) our approach is growing nanostructured metal oxide on 3D interconnected graphene networks with high surface area and high electronic conductivity.

specific capacitances of 148–410 F/g have been achieved, such values were obtained only under slow charge–discharge rates and they were found to decrease rapidly as the discharge rate was increased. Moreover, many of these materials have low packing density with large pore volume, meaning that a huge amount of electrolyte is needed to build the device, which adds to the mass of the device without adding any capacitance (25). Accordingly, the energy density and power density of these systems are very limited on the device level. To solve these critical problems, we have developed promising hybrid electrodes based on 3D graphene doped with MnO_2 nanoflowers. By rationally designing the structure of the graphene substrate to achieve high conductivity, suitable porosity, and high specific surface area, one may expect to not only achieve a high gravimetric capacitance, but also to improve the volumetric capacitance (23). Furthermore, the high surface area of nanostructured MnO_2 provides more active sites for the Faradaic reactions and shortens the ion diffusion pathways that are crucial for realizing its full pseudocapacitance. We show that hybrid supercapacitors based on these materials can achieve energy densities of up to 42 Wh/l compared with 7 Wh/l for state-of-the-art commercially available carbon-based supercapacitors. Interestingly, these graphene–MnO_2 hybrid supercapacitors use aqueous electrolytes and are assembled in air without the need for the expensive dry rooms required for building today's supercapacitors.

Whereas great efforts have been made for the fabrication of macroscale hybrid supercapacitors, there are only a few studies on the design and integration of hybrid materials into microsupercapacitors (26). This is likely due to complicated microfabrication techniques that often involve building 3D microelectrodes with micrometer separations. Here, we present a simple, yet versatile technique for the fabrication of 3D hybrid microsupercapacitors based on graphene and MnO_2. These microdevices enable an ultrahigh capacitance per footprint approaching 400 mF/cm^2, which is among the highest values achieved for any microsupercapacitor (26). They can also provide an energy density of up to 22 Wh/l, more than two times that of lithium thin-film batteries. These developments are promising for microelectronic devices such as biomedical sensors and radiofrequency identification tags where high capacity per footprint is crucial.

Results

In designing supercapacitor electrodes, special efforts are made to ensure that they are capable of providing high energy density and high power density. This requires optimization of the preparation conditions to facilitate ionic and electronic transport within the electrodes (27) as illustrated in Fig. 1 (see also *SI Appendix*, section 1).

Synthesis and Characterization of 3D Macroporous Laser-Scribed-Graphene–MnO_2 Electrodes. To experimentally realize energy-dense and high-power supercapacitor electrodes, we integrated a highly conductive and high-surface-area 3D laser-scribed graphene (LSG) framework with MnO_2 as schematically illustrated in Fig. 2*A*. The 3D LSG framework was produced from the laser scribing of GO films following our previously reported method (27), upon which the color changes from golden brown to black. The LSG framework was subsequently coated in situ with MnO_2 using an electrochemical deposition technique as described in *Materials and Methods*; Fig. 2*B*. Note in Fig. 2*B* that the graphene electrode turns darker in color after electrodeposition, a visual indication of the loading of MnO_2. It is well accepted that the conductivity and mass loading of the active materials have a significant impact on the electrochemical behavior of supercapacitor electrodes. Here, the mass loading of MnO_2 is controlled by adjusting the deposition current and deposition time. Fig. 2*C* shows that the MnO_2 loading changes almost linearly with the deposition time at an applied current of 0.25 mA/cm^2 and an average deposition rate estimated to be ~6 μg/min.

In addition to interesting electrical properties, the LSG–MnO_2 electrodes are monolithic and demonstrate superb mechanical integrity under large mechanical deformation. Fig. 2*D* shows that an LSG–MnO_2 electrode can be bent significantly without damage. We evaluated the foldability of LSG–MnO_2 electrodes by measuring their electrical resistance under successive bending cycles. The resistance varies only slightly up to a bending radius of 5.0 mm and can be completely recovered after straightening no matter whether the bending is positive (convex) or negative (concave). Notably, after 1,000 cycles of bending and straightening at a concave bend radius of 5.0 mm, the resistance has increased by only about 2.8%; Fig. 2*E*.

Fig. 2. Fabrication and characterization of LSG/MnO_2 electrodes. (*A*) Schematic diagram presents the fabrication procedure for the LSG–MnO_2 electrodes. (*B*) Digital photographs show a GO film before and after laser scribing. The LSG is then loaded with MnO_2, whose amount can be controlled by adjusting the deposition time from 3 to 120 min. (*C*) Mass loading of MnO_2 versus deposition time. (*D*) Variation of the resistance of an LSG–MnO_2 electrode as a function of bending radius. (*E*) Resistance change of an LSG–MnO_2 electrode under repeated bending cycles for a concave bend radius of 5 mm. (*Inset*) Photograph showing the flexibility of an LSG–MnO_2 electrode.

Fig. 3. Morphological and structural characterization of LSG–MnO_2 electrodes. (*A* and *B*) SEM images of an LSG–MnO_2 electrode at low and high magnification. (*C*) SEM image shows the nanoflower morphology of electrodeposited MnO_2. (*D*) Cross-sectional SEM image of an LSG–MnO_2. (*E*) EDS elemental mapping of C (red), Mn (blue), and O (green). (*F*) XPS spectra of Mn 2p showing a doublet with a peak-to-peak separation of 11.6 eV. (*G*) XPS spectra of Mn 3s.

The evolution of morphology corresponding to different deposition times was examined by scanning electron microscopy (SEM); Fig. 3 *A*–*D*. The SEM micrographs show the general morphology and detailed microstructure of a typical sample prepared by 120 min of deposition. MnO_2 has been uniformly coated onto the surface of graphene throughout the entire film. Moreover, the electrodeposited MnO_2 particles show a nanoflower-shaped hierarchical architecture with a clear interface between MnO_2 and the graphene substrate which is consistent with previous studies (20). Closer inspection of the MnO_2 nanoflowers shows that they are made up of hundreds of ultrathin nanoflakes that are 10–20 nm thick (see also *SI Appendix*, Fig. S3). These nanoflakes are interconnected together to form mesoporous MnO_2 with a large accessible surface area, thus offering numerous electroactive sites available to the electrolyte which promotes fast surface Faradaic reactions.

The 3D structure of LSG–MnO_2 electrodes was further analyzed using cross-sectional SEM; Fig. 3*D*. The 3D porous structure of LSG is preserved after the deposition of MnO_2 without any agglomerations. The graphene surface has been uniformly coated with MnO_2 over the entire cross-section. In addition, energy-dispersive X-ray spectroscopy (EDS) provides elemental maps of C, O, and Mn, which confirms that a homogeneous coating of MnO_2 throughout the 3D macroporous framework has been created. The X-ray photoelectron spectroscopy (XPS) data shown in Fig. 3 *F* and *G* further confirm the chemical composition of the deposited oxide; see *SI Appendix* for details.

Assembly and Electrochemical Performance of Symmetric LSG–MnO_2 Supercapacitors. To test the electrochemical performance of LSG–MnO_2 macroporous frameworks, a supercapacitor pouch cell was assembled from two symmetric electrodes separated by a Celgard M824 ion porous separator and impregnated with 1.0 M Na_2SO_4 electrolyte; Fig. 4*A*. The cells were tested by cyclic voltammetry (CV) over a wide range of scan rates from 1 to 1,000 mV/s. As an example, consider the LSG–MnO_2 sample with a deposition time of 3 min: the supercapacitor shows nearly rectangular CV profiles up to a scan rate as high as 1,000 mV/s, indicating excellent charge storage characteristics and ultrafast response time for the electrodes; Fig. 4*B*. The capacitances of the devices made with different deposition times were calculated from CV profiles and are presented in Fig. 4*C*. Note that the capacitance was calculated using the total volume of the cell stack, rather than a single electrode. This includes the volume of the current collector, the active material, the separator, and the electrolyte.

We observe that the capacitance depends strongly on the loading amount of the pseudocapacitive MnO_2 and increases significantly with deposition time from 0 to 960 min. For example, a stack capacitance of up to ~203 F/cm^3 can be achieved with the sample at a 960-min deposition time. This translates to a volumetric capacitance of 1,136.5 F/cm^3 when calculated based on the volume of the active material per electrode only. This value is much higher than the capacitance of activated carbons (60–80 F/cm^3), carbide-derived carbons (180 F/cm^3), bare LSG (12 F/cm^3), activated microwave exfoliated graphite oxide (60 F/cm^3), and liquid-mediated chemically converted graphene (CCG) films (263.3 F/cm^3), indicating that the volumetric capacitance of carbon-based electrodes can be significantly improved by incorporating pseudocapacitive materials (*SI Appendix*, Table S1). Furthermore, this value is higher than some of the best values reported previously for MnO_2-based supercapacitors: 16.1 F/cm^3 for carbon nanotube-polypyrrole–MnO_2 sponge, 130 F/cm^3 for graphene–MnO_2–CNT, 246 F/cm^3 for CNT–MnO_2, 108 F/cm^3 for

Fig. 4. Electrochemical performance of LSG–MnO_2 symmetric supercapacitors. (*A*) Schematic of the device. (*B*) CV profiles for an LSG–MnO_2 (3 min) supercapacitor at different scan rates. (*C*) Evolution of the stack capacitance of LSG with various mass loadings of MnO_2 as a function of scan rate. (*D*) Specific capacitance due to MnO_2 only as a function of the loadings measured at a scan rate of 1 mV/s. (*E*) Charge–discharge curves of an LSG–MnO_2 (3 min) supercapacitor at different current densities. (*F*) Change of stack capacitance of an LSG–MnO_2 (120 min) supercapacitor as a function of current density. Data for CCG–MnO_2 (120 min) and Au–MnO_2 (120 min) supercapacitors are presented for comparison. (*G* and *H*) Progression of the real (C′) and imaginary (C″) parts of the stack capacitance of CCG (*G*) and LSG (*H*) as a function of frequency. (*I*) Comparison of the LSG–MnO_2 (120 min) hybrid capacitor with a commercially available activated carbon supercapacitor (2.7 V/10 F), pseudocapacitor (2.6 V/35 mF), and a lithium-ion hybrid capacitor (2.3 V/220 F).

Fig. 5. Asymmetric supercapacitor based on graphene–MnO_2 as the positive electrode and LSG as the negative electrode. (*A*) Schematic showing the structure of the assembled supercapacitor in 1.0 M Na_2SO_4 electrolyte. (*B* and *C*) Electrochemical performance of the asymmetric supercapacitor after increasing the potential window from 0.8 to 2.0 V. (*D*) Change of the stack capacitance as a function of current density. (*E*) Electrochemical performance of the device under different bending angles. (*F*) Cycling stability of the device tested over 10,000 cycles at a scan rate of 1,000 mV/s. Change of the ESR during cycling is also shown.

mesoporous carbon/MnO_2, and 90 F/cm^3 for ultraporous carbon–MnO_2. In addition, depending on the deposition time, ultrahigh areal capacitances of up to ~0.8 F/cm^2 per footprint of the device can be achieved. This compares favorably with commercial carbon supercapacitors that typically provide ~0.3 F/cm^2.

This unprecedented performance can be understood by separating the contribution of the MnO_2 nanoflowers from the average capacitance of the LSG–MnO_2 electrodes. The specific capacitance of MnO_2 depends on the mass of the active material reaching a maximum value of 1145 F/g, which is about 83% of the theoretical capacitance at a mass loading of 13% of MnO_2; Fig. 4*D*. This remarkable performance can be attributed to the electrode microstructure that facilitates the transport of ions and electrons and provides abundant surfaces for charge–transfer reactions, ensuring a greater utilization of the active materials.

To demonstrate the superior properties of LSG–MnO_2 macroporous electrodes, MnO_2 was also electrodeposited on both CCG and gold substrates under the same conditions and their electrochemical performance is presented in Fig. 4*F*. Not only does the CCG–MnO_2 exhibit lower capacitance, but its performance falls off very quickly at higher charge–discharge rates. This can be attributed to the restacking of graphene sheets during the fabrication of the CCG electrodes, resulting in a significant reduction in the surface area and eventually closing off much of the porosity (28). In addition, the Au–MnO_2 supercapacitor shows extremely low capacitance because of the limited surface area and structural properties as can be seen in Fig. 1*A*. LSG–MnO_2, on the other hand, shows a stack capacitance of ~50 F/cm^3 that is more than four times higher than CCG–MnO_2 and about three orders of magnitude higher than Au–MnO_2. The enhanced capacitance and rate capability of the LSG–MnO_2 further confirms its optimized structure, which synergizes the effects of both effective ion migration and high electroactive surface area, thus enabling high and reversible capacitive behavior even at high charge–discharge rates. The optimized ionic diffusion of the LSG network was also confirmed from electrochemical impedance spectroscopy with a response time of 23 ms for LSG compared with 5,952 ms for the CCG electrodes; Fig. 4 *G* and *H*) (see also *SI Appendix*, section 2 and Figs. S1 and S2). In fact, the LSG–MnO_2 supercapacitor shows superior volumetric capacitance and rate capability compared with commercially

Fig. 6. Engineering of 3D interdigitated microsupercapacitors with high energy density. (*A*–*C*) Illustration of the fabrication process for an asymmetric microsupercapacitor based on LSG–MnO_2 as the positive electrode and LSG as the negative electrode. (*D*) Photograph showing the asymmetric microsupercapacitor. (*E*) Optical microscope image showing the LSG–GO–LSG-MnO_2 interface. (*F*) SEM image of the interface between GO and LSG shows the selective electrodeposition of MnO_2 on LSG only. (*Inset*) Magnified view of the GO and LSG area. (*G*–*I*) Comparison of the stack capacitance of the supercapacitor between the sandwich structure and the planar interdigitated structure for (*G*) asymmetric, MnO_2 deposition time 3 min and (*H* and *I*) symmetric devices.

Fig. 7. Ragone plot comparing the energy and power density of LSG–MnO_2 supercapacitors with a number of commercially available energy storage devices: a lead acid battery, a lithium thin-film battery, an aluminum electrolytic capacitor, activated carbon supercapacitors of variable sizes, a pseudocapacitor, and a lithium-ion hybrid capacitor. Performance data for Au–MnO_2 and CCG–MnO_2 are also included to demonstrate the importance of the microstructure of the electrodes.

available activated carbon supercapacitors, pseudocapacitors, and lithium-ion hybrid capacitors as can be seen from Fig. 4*I*.

Construction of Asymmetric Supercapacitors. Considering the high pseudocapacitance of the LSG–MnO_2 electrode and the fast charge–discharge of the double-layer capacitance of the LSG electrode, an asymmetric supercapacitor was assembled using LSG–MnO_2 as the positive and LSG as the negative electrode, as schematically illustrated in Fig. 5*A* (see also *SI Appendix*, section 3). Here, a charge balance between the two electrodes was achieved by controlling the deposition time of MnO_2 at the positive electrode and the thickness of the graphene film at the negative electrode. The electrochemical performance of an asymmetric cell that uses LSG–MnO_2 with 13% MnO_2 mass loading (3-min deposition time) for the positive electrode is shown in Fig. 5 *B* and *C*. The cell exhibits an ideal capacitive behavior with nearly rectangular CV profiles and highly triangular charge/discharge curves; Fig. 5 *B* and *C*. The CV profiles retain their rectangular shape without apparent distortions with increasing scan rates up to an ultrahigh rate of 10,000 mV/s, indicating the high rate capability of this asymmetric supercapacitor. Interestingly, the asymmetric cell presents a wide and stable operating potential window up to 2.0 V in aqueous electrolyte that should afford high energy density. Furthermore, as the MnO_2 deposition time is increased from 3 to 960 min, the stack capacitance increases significantly from around 3 to 76 F/cm^3, meaning that the stored energy and power can be greatly improved in the asymmetric structure; Fig. 5*D*. These cells can also retain their high capacity when faster charge and discharge rates are needed. In addition, the as-fabricated supercapacitor is highly flexible and can be folded and twisted without affecting the structural integrity of the device or its electrochemical performance, holding promise as a practical energy storage system for flexible electronics; Fig. 5*E*.

Long cycle life is another important feature for commercially viable supercapacitors. Indeed, the asymmetric supercapacitor is very stable as it maintains over 96% of its original capacity after 10,000 charge–discharge cycles tested at a high scan rate of 1,000 mV/s; Fig. 5*F*. The equivalent series resistance (ESR) of the supercapacitor was monitored during cycling using a Nyquist plot. The device demonstrates a slight increase of ESR in the first 1,000 cycles with only subtle changes over the remaining cycles.

Three-Dimensional Interdigitated Microsupercapacitors. The development of microsupercapacitors with high capacity per footprint area is crucial for the miniaturization of energy storage devices for modern electronic applications (26). Unfortunately, current state-of-the-art systems still suffer from low areal capacity (26): <11.6 mF/cm^2 for carbons (29, 30), <78 mF/cm^2 for conducting polymers (31), and <56.3 for metal oxides (32). We designed new hybrid microsupercapacitors as illustrated in Fig. 6 *A–C*, in which the positive and negative electrodes are separated into a 3D interdigitated structure. This structure was achieved by combining the techniques of "top-down" LightScribe lithography with "bottom-up" selective electrodeposition. First, 3D interdigitated LSG microelectrodes were produced by the direct writing of graphene patterns on GO films using a consumer-grade LightScribe DVD burner. Subsequently, MnO_2 nanoflowers were selectively electrodeposited on one set of the LSG microelectrodes using the cell setup described in the schematic diagram (*Materials and Methods*). The width of the microelectrodes is adjusted to match the charge between the positive and negative poles of the microdevice. Fig. 6*D* shows a digital photograph of an asymmetric microsupercapacitor that consists of alternating positive and negative electrodes. The lighter microelectrodes correspond to bare graphene (negative electrodes), whereas the other side turns darker in color after the electrodeposition of MnO_2 (positive electrodes). The optical microscope image shows a well-defined pattern and sharp boundaries between the microelectrodes; Fig. 6*E*. SEM further confirmed the conformal structure of this asymmetric microsupercapacitor. A magnified view at the interface between GO and graphene shows the selective electrodeposition of MnO_2 on the graphene area only; Fig. 6*F*.

Electrochemical characterization shows that the asymmetric microsupercapacitor provides enhanced volumetric capacitance and rate capability compared with a conventional sandwich-type asymmetric supercapacitor; Fig. 6*G*. Symmetric hybrid microsupercapacitors show a similar behavior (Fig. 6 *H* and *I*), with the areal capacitance approaching 400 mF/cm^2. To the best of our knowledge, this is the highest areal capacitance achieved so far in an interdigitated microsupercapacitor. The stack capacitance significantly improves to ~250 F/cm^3 (volumetric capacitance per electrode is 1,197 F/cm^3), which is much higher than values previously reported for EDLC, pseudo-, and hybrid microsupercapacitors: 1.3 F/cm^3 for carbon onions, 2.35–3.05 F/cm^3 for graphene, 1.08 F/cm^3 for CNT, 3.1 F/cm^3 for graphene–CNT, 180 F/cm^3 (electrode) for carbide-derived carbon, 588 F/cm^3 for polyaniline nanofibers, 317 F/cm^3 (electrode) for vanadium

Fig. 8. Direct fabrication of supercapacitor arrays for high-voltage applications and integrated energy storage. (*A*) Direct fabrication of an asymmetric supercapacitor array consisting of 9 cells in a single step. Charge–discharge curves of asymmetric supercapacitor arrays connected in series (3 cells in series, 3S), in parallel (3 cells in parallel, 3P), and in a combination of series and parallel (3 series × 3 parallel, 3S × 3P). A single device is shown for comparison. (*B*) Integration of a supercapacitor array with solar cells for efficient solar energy harvesting and storage.

disulfide nanosheets, and 178 F/cm^3 for molybdenum disulfide nanosheets (*SI Appendix*, Table S2).

Discussion

The energy and power density of the LSG–MnO_2-based supercapacitors are presented in Fig. 7. To put these results in perspective with current technology, we characterized a number of commercially available carbon-based supercapacitors, pseudocapacitors, hybrid supercapacitors, and Li-ion hybrid capacitors and the results are presented in the same plot. These devices were tested under the same dynamic conditions as LSG–MnO_2. For all devices, the calculations were made based on the volume of the full cell that includes the current collector, active material, separator, and electrolyte. The energy density of the hybrid LSG–MnO_2 varies between 22 and 42 Wh/l depending on the configuration (symmetric, asymmetric and sandwich, interdigitated) and the mass loading of MnO_2. By comparison, the LSG–MnO_2 hybrid supercapacitors store about 6 times the capacity of state-of-the-art commercially available EDLC carbon supercapacitors. They are also superior to pseudocapacitors, hybrid supercapacitors, and supercapacitor–lithium-ion battery hybrid (Li-ion capacitors). Furthermore, LSG–MnO_2 supercapacitors can provide power densities up to ∼10 kW/l, which is 100 times faster than high-power lead acid batteries and 1,000 times faster than a lithium thin-film battery.

To meet the high voltage requirements, supercapacitors are often put into a bank of cells connected together in series. This results in bulky supercapacitor modules, which are appropriate in some cases but often cause problems in applications where the total size of the power source is critical. Here, we propose a different design in which an array of separate electrochemical cells is directly fabricated in the same plane and in one step as shown in Fig. 8*A* (see also *SI Appendix*, sections 4, 5 and Figs. S4–S8). This configuration shows very good control over the voltage and current output. In addition, this array can be integrated with solar cells for efficient solar energy harvesting and storage, as shown in Fig. 8*B* and *SI Appendix*, Movie S1.

In summary, we have developed a simple and scalable approach for the fabrication of hybrid LSG–MnO_2 3D supercapacitors and microsupercapacitors that are compact, reliable, and energy dense, charge quickly, and possess long lifetime. Given that MnO_2 is widely used in alkaline batteries [selling ∼10 billion units per year (33)] and the scalability of graphene-based materials, we believe that graphene–MnO_2 hybrid electrodes offer promise for real-world applications.

Materials and Methods

Synthesis of LSG–MnO_2, Au–MnO_2, and CCG–MnO_2 Electrodes. The LSG framework was prepared by focusing a laser beam from a LightScribe DVD burner on a DVD disk coated with graphite oxide. First, the DVD disk is covered by a film of gold-coated polyimide (Astral Technology Unlimited, Inc.) or a sheet of polyethylene terephthalate. This was coated with a 2% GO dispersion in water using the doctor blade technique and left for drying for 5 h under ambient conditions. A computer-designed image is printed onto graphite oxide to make the appropriate LSG pattern (27). This was followed by the electrodeposition of MnO_2 from 0.02 M $Mn(NO_3)_2$ in 0.1 M $NaNO_3$ aqueous solution using a standard three-electrode setup, where a piece of LSG (1 cm^2) is used as the working electrode, Ag–AgCl as the reference electrode (BASi), and a platinum foil (2 cm^2, Sigma-Aldrich) as the counter-electrode. The deposition was achieved by applying a constant current of 250 μA/cm^2 for different time periods between 3 and 960 min. For more information on the assembly of supercapacitors, microsupercapacitors, and characterization methods, please see *SI Appendix, Materials and Methods*.

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Supporting Information

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Movie S1. LSG/MnO_2 hybrid supercapacitors can be integrated with solar cells in one unit for efficient solar energy conversion and storage.

Movie S1

Other Supporting Information Files

SI Appendix (PDF)

SUPPORTING INFORMATION

Engineering Three-Dimensional Hybrid Supercapacitors and Micro-Supercapacitors for High-Performance Integrated Energy Storage

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1. Rational design of high-performance hybrid supercapacitors. To achieve high-energy and high-power supercapacitors, one needs to facilitate both the ionic and electronic currents within the electrodes. This is very challenging especially with metal oxide pseudo-capacitors because of the low electrical conductivity and long ionic diffusion pathways of conventional metal oxide films. Thus, in conventional compact MnO_2 thick film electrodes, only the top layer is exposed to the electrolyte, meaning that a limited amount of the active material is involved in charge storage, Fig. 1A. To solve these problems, various approaches have been explored in the literature. For example, the electrochemical utilization of electrodes was improved by using nanostructured MnO_2 such as nanoparticles, nanorods, nanowires and nanoflowers [1-2]. The porous structure of these electrodes maximizes the area of active material that is exposed to the electrolyte and thus available to discharge compared to a solid electrode surface, Fig. 1B. Although this system exhibits higher energy density, it still suffers from the inherently low electrical conductivity of MnO_2 leading to low power output. To improve the electrical conductivity of MnO_2 film, conductive materials such as carbon powder, carbon nanotubes and graphene have been introduced into nanostructured MnO_2 electrodes [3]. However, the electronic charge carriers must move through small inter-particle contact areas which exhibit additional resistance resulting in poor electron transport from the electrode material to the current collector, Fig. 1C. An ideal electrode would be obtained by growing MnO_2 nanostructures onto a 3D interconnected macro-porous graphene framework with high electrical conductivity and high surface area, Fig. 1D. In this structure, the conducting graphene framework acts as a 3D current collector to provide electron "superhighways" for charge storage and delivery, while the nanostructured MnO_2 enables fast, reversible Faradaic reactions with short ionic diffusion pathways. Another interesting feature of this structure is that each MnO_2 nanoparticle is electrically connected to the current collector so that all the nanoparticles contribute to capacity with almost no "dead" mass.

2. Graphene/metal oxide nanocomposites: The microstructure of the host graphene matters!

Does the pore structure of the graphene electrode affect the electrochemical performance of its composites with metal oxides? To answer this question, we employed two forms of graphene of different pore structures in this study: chemically converted graphene (CCG) films and laser scribed graphene (LSG) films. The CCG sheets are well connected together in a layered structure to form the CCG electrodes. The reduced porosity and limited accessibility to electrolyte ions causes a slow frequency response of ~5 seconds for CCG electrodes (Figure S1). LSG electrodes, on the other hand, have a well-defined porous structure such that the individual graphene sheets in the LSG network are accessible to the electrolyte, and thus exhibit a rapid frequency response of 23 ms (Figure S2). This causes the enhanced capacitance and rate capability observed with the LSG/MnO_2. The optimized structure of LSG electrodes synergizes the effects of both effective ion migration and high electroactive surface area, thus enabling high and reversible capacitive behavior for LSG/MnO_2 even at high charge/discharge rates.

Further understanding of the capacitive behavior of the CCG/MnO_2 and LSG/MnO_2 hybrid electrodes was obtained by conducting ac impedance measurements in the frequency range 1 MHz to 10 mHz. For each of these cells, MnO_2 was electrodeposited for 120 min. The Nyquist plots consist of a spike at the low frequency region and a semicircle at the high frequency region (Figure S2). Compared with CCG/MnO_2, the LSG/MnO_2 supercapacitor shows a much smaller diameter for the semicircle, which suggests a more efficient charge transfer on the electrode surface. Furthermore, in the low frequency region, a more vertical straight line is observed for the porous LSG/MnO_2 electrodes, indicating faster ion diffusion and almost ideal capacitive behavior for these electrodes. The intercept of the Nyquist curve on the real axis is about 1.5 Ω, indicating a high conductivity for the electrolyte and low internal resistance of the electrodes (Figure S2). These results show the strong impact of the microstructure of the graphene electrodes on the electrochemical performance of their composites with metal oxides.

The LSG/MnO_2 has just the right porosity that provides good accessibility to the electrolyte during charge and discharge processes, while at the same time still maintains the high packing density of the material. Furthermore, the high surface area of nanostructured MnO_2 provides more active sites for the Faradaic reactions and shortens the ion diffusion pathways that are crucial for realizing its full pseudo-capacitance. This explains why the LSG/MnO_2 electrodes achieve both high gravimetric capacitance and volumetric capacitance superior to those previously reported for MnO_2 based pseudo-capacitors and hybrid capacitors, see table S1.

Figure S1: Effect of the pore structure of graphene on its electrochemical performance. Top: Schematic illustration showing the structural differences between dense CCG films and porous LSG films. Bottom: The emergence of real (C') and imaginary (C'') parts of the volumetric stack capacitance versus frequency for CCG and LSG electrodes.

Figure S2: Nyquist impedance plots of CCG/MnO_2 and LSG/MnO_2. The LSG/MnO_2 shows better ion diffusion and smaller charge transfer resistance. The experiments were carried out over a frequency range of 1 MHz to 10 mHz.

Figure S3: Evolution of the surface of LSG/MnO_2. SEM analysis of the surface of LSG/MnO_2 electrodes shows a homogeneous coating of the surface of graphene with MnO_2 nanoflowers.

3. Asymmetric Supercapacitors: Asymmetric supercapacitors make use of positive and negative electrode materials of different types that can be charged/discharged in well-separated potential windows in the same electrolyte. They have attracted attention because they offer high capacity via a Faradaic reaction at the positive electrode and maintain fast charge/discharge due to the EDL mechanism at the negative electrode. Moreover, the asymmetric configuration can extend the operating voltage window of aqueous electrolytes beyond the thermodynamic limit of water (about 1.2 V), leading to significantly higher specific energy than symmetric supercapacitors using aqueous electrolytes. In fact, asymmetric supercapacitors based on carbon and NiOOH electrodes with an aqueous electrolyte are now commercially available from ESMA-ELTON (4). However, while this configuration ensures high capacitance, it has a low cell voltage (<1.5 V) that is detrimental to its energy and power performance.

4. Direct fabrication of hybrid micro-supercapacitor array for high voltage applications.

Supercapacitors are widely used in a variety of applications where a large amount of power is needed for a short period of time, where a very large number of charge/discharge cycles or a longer lifetime is required. However, the working voltage of existing supercapacitors is very low (<3 volts), whereas traditional capacitors used for general electronics applications typically range from a few volts to 1 kV. To meet the high voltage requirements, supercapacitors are often put into a bank of cells connected together in series (5). This results in bulky supercapacitor modules which are appropriate in some cases, but often cause problems in applications where the total size of the power source is critical. Here, we propose a different design in which an array of separate electrochemical cells are directly fabricated in the same plane as shown in Figures S4-S8.

First, circuits are designed using appropriate computer software and are directly patterned on a graphite oxide film coated on a DVD disc. Figure S4 shows a DVD after the direct writing of LSG patterns designed to achieve symmetric and asymmetric micro-supercapacitor arrays. It is also

possible to design patterns to make a supercapacitor bank of series/parallel combinations in order to meet the voltage (series) and current (parallel) requirements of the system on which they will be integrated.

The second step is the deposition of MnO_2 nanoflowers. Here, the deposition process varies depending on whether it is a symmetric or an asymmetric array. For an asymmetric array, the process is explained in Figures S5-S6 and for a symmetric array in Figure S7. A full set of symmetric and asymmetric supercapacitor arrays are shown in Figure S8 and their electrochemical performance in Figure S9. Ideally a gel electrolyte is used to prevent leakage into other cells in the array.

These arrays offer the flexibility of controlling the output voltage and current of the array. For example, compared with a single device with an operating voltage of 2 V, an array of 3 serial cells extends the output voltage to 6 V, whereas the output capacity (runtime) can be increased by a factor of 3 using an array of 3 cells connected in parallel (Fig. S9). By using an array of 3 strings in parallel and 3 strings in series, the output voltage and current can both be tripled. Although we demonstrated the high-voltage supercapacitor array using a string of 3 cells, it is possible to increase the number of cells to reach an operating voltage of 100 V, which would be promising for a variety of applications.

5. Integration of Micro-supercapacitor array with solar cells for simultaneous solar energy harvesting and storage.

With growing interest in "green" systems, solar power is gaining popularity for the implementation in more energy efficient buildings and smart cities. When combined with an energy storage system for storing energy during the day, they can be used to make self-powered systems that are promising for streetlight, industrial wireless monitoring, transportation and consumer

electronics applications (6). Chemical batteries are often used in these systems due to their high energy density. Recently, supercapacitors are emerging as alternatives because they can capture energy more efficiently due to their short response time. These modules are struggling, though, because of the low energy density of existing supercapacitors. Since LSG/MnO_2 hybrid supercapacitors can provide higher energy density and because they can be fabricated in arrays with high voltage and current ratings, they can be integrated with solar cells for highly efficient energy harvesting and storage (Fig. 8b).

Figure S4: LightScribe writing of LSG micro-supercapacitor arrays: The pattern is designed with Microsoft Paint software and then directly patterned on a GO coated DVD disc. The device consists of 8 in-plane microelectrodes (4 positive and 4 negative) separated by nearly insulating GO and the distance between the microelectrodes is close enough to keep the ion-transport pathway short.

Figure S5: Fabrication of an array of 9 asymmetric cells connected in series/parallel: The plain graphene array is first made as explained in Figure S4. In this example, the graphene pattern is designed to make an array of 9 cells (3 in parallel X 3 in series). This is followed by the electro-deposition of MnO_2 in a three electrode cell as schematically illustrated in the figure. Since this is an asymmetric supercapacitor, the deposition is controlled to go on three sets of micro-electrodes (the positive electrodes) and the other three are kept intact (negative electrodes). It is worth mentioning that the MnO_2 deposition occurs on the 9 cells at the same time. This means that the fabrication of the supercapacitor array takes almost the same time as a single cell without the need for further processing. After the deposition is complete, the supercapacitor array is thoroughly washed with DI water and the electrolyte is added onto each of the cells. The full micro-supercapacitor array is shown in Figure S6.

Figure S6: The finished array of 9 asymmetric cells connected 3 in series X 3 in parallel.

Figure S7: Fabrication of an array of 9 symmetric supercapacitors connected in series/parallel. The fabrication method is similar to that explained in Figure S5 except that all six sets of micro-supercapacitor electrodes act as the working electrode during the deposition of MnO_2 instead of the three shown in Figure S5.

Figure S8: Demonstration of supercapacitor arrays that are connected in series, parallel and in combinations of the two. This can be done for both symmetric and asymmetric cells.

Figure S9: The electrochemical performance of asymmetric supercapacitor arrays. Galvanostatic charge/discharge curves of asymmetric supercapacitor arrays connected in series (3S), in parallel (3P), and in a combination of series and parallel (3S x 3P). A single device is shown for comparison. Compared with the single device with an operating voltage of 2 V, the serial connection extends the output voltage to 6 V, whereas the output capacity (runtime) can be increase by a factor of 3 using the parallel connection. By using a combination of series/parallel connections, the output voltage and current can both be tripled.

Electrode Material	Cell Type	Voltage window	Electrolyte	Specific capacitance		Ref.
				Per Footprint area (mF/cm^2)	Volumetric (F/cm^3)	
Activated carbons	Full cell	2.7 V	$TEABF_4$/AN	~300	60-80	7
Carbide derived carbon	3 electrode	2.3 V	$TEABF_4$/AN	–	180	8
LSG	Full cell	4.0 V	$EMIMBF_4$	5.02	14.34	9
Activated MEGO	Full cell	3.5 V	BMIM-BF_4/AN	–	60	10
Liquid mediated CCG	Full cell	3.5 V	$EMIMBF_4$/AN	–	263.3	11
CNT/PPy/MnO_2	Full cell	0.9 V	KCl	–	16.1	12
Graphene/MnO_2/CNT	Full cell	1.0 V	1.0 M Na_2SO_4	–	130	13
CNT/MnO_2	3 electrode	0.85 V	0.1 M K_2SO_4	–	246	14
Meso-porous carbon/MnO_2	3 electrode	0.8 V	1.0 M Na_2SO_4	–	108	15
Ultra-porous Carbon/MnO_2	3 electrode	0.8 V	1.0 M Na_2SO_4	1500*	90	16
Graphene/RuO_2	3 electrode	1.0 V	1.0 M H_2SO_4	–	(570 F/g)#	17
CNT/Co_3O_4	3 electrode	0.5 V	2.0 M KOH	30.8	30.8	18
Titanium carbide clay	3 electrode	0.55 V	1.0 M H_2SO_4	–	910 @5 µm 534 @30 µm 355 @75 µm	19
MXene/PVA	3 electrode	0.6 V	1.0 M KOH	–	528	20
LSG/MnO_2 (15 µm thick film)	Full cell	0.9 V	1.0 M Na_2SO_4	852	1136.5	This work

Table S1: Electrochemical performance of supercapacitors featuring a variety of electrodes materials such as carbons, polymers, MnO_2 and their hybrid materials. AN: Acetonitrile; $TEABF_4$: tetraethylammonium tetrafluoroborate; $EMIMBF_4$: 1-ethyl-3-methylimidazolium tetrafluoroborate; $BMIMBF_4$: 1-butyl-3-methyl-imidazolium tetrafluoroborat. # Since the volumetric capacitance is not reported, we use the gravimetric capacitance instead. *notice that the capacitance per footprint area in 3 electrode measurements is at least two times the areal capacitance for 2 electrode measurements (21).

Electrode Material	Cell Type	Voltage window	Electrolyte	Specific capacitance		Ref.
				Per Footprint area (mF/cm^2)	Volumetric (F/cm^3)	
Carbon onions	Full cell	3.0 V	$TEABF_4$/PC	1.7	1.35	22
Graphene	Full cell	1.0 V	PVA-H_2SO_4	2.32	3.05	23
Graphene	Full cell	2.5 V	Ionogel*	1.78	2.35	23
Graphene-CNT carpet	Full cell	1.0 V	1.0 M Na_2SO_4	2.16	1.08	24
Graphene/CNT	Full cell	1.0 V	3.0 M KCl	5.1	3.1	25
Carbide-derived carbon	Full cell	2.3 V	$TEABF_4$/AN	–	180	8
Polyaniline nanowires	Full cell	1.0 V	1.0 M H_2SO_4	–	588	26
Activated cabon-MnO_2	Full cell	1.0-1.5 V	0.2 M K_2SO_4	21.3-30	–	27
MnO_2	Full cell	1.0 V	0.2 M K_2SO_4	28.3	–	27
VS_2 nanosheets	Full cell	0.6 V	PVA–$BMIMBF_4$	4.76	317	28
MoS_2 nanosheets	Full cell	0.5 V	–	8	178	29
LSG/MnO_2	Full cell	0.9 V	1.0 M Na_2SO_4	384	1136.5	This work

Table S2: Electrochemical performance of interdigitated micro-supercapacitors. *Ionogel: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid gelled with fumed silica nanopowder.

SI Materials and Methods

After electro-deposition, the working electrode was thoroughly washed with DI water to remove the excess electrolyte and dried in an oven at 60 °C for 1 h. The amount of MnO_2 deposited on the LSG framework was determined from the difference in weight of the electrode before and after electro-deposition using a high precision microbalance with a readability of 1 μg (Mettler Toledo, MX5).

For comparison, MnO_2 was electrodeposited on other substrates such as gold-coated polyimide and graphene (CCG) paper. The gold-coated polyimide was obtained from Astral Technology Unlimited, Inc. (Minnesota, USA) and used without further treatment. The graphene paper was produced following our previously reported method (30). The gold-coated polyimide and graphene paper were cut into rectangular strips of 1 cm^2 for further electro-deposition of MnO_2 under the same conditions as described above.

Assembly of sandwich-type hybrid supercapacitors. Hybrid supercapacitors with the conventional sandwich structure were assembled using electrodes prepared in the previous section. Both symmetric and asymmetric supercapacitors were constructed. Symmetric supercapacitors were assembled by sandwiching a Celgard M824 (Celgard, North Carolina, USA) separator between two identical electrodes using 1.0 M Na_2SO_4 aqueous solution as the electrolyte. In the asymmetric structure, LSG/MnO_2 was used as the positive electrode and LSG as the negative electrode. For the LSG- and CCG-based supercapacitors, stainless steel (or copper) tape was attached to the electrodes, using silver paint, as the current collector. Before assembly, the electrodes were soaked in the electrolyte for 1 h to ensure proper wetting.

Fabrication of interdigitated hybrid micro-supercapacitors. The fabrication process of a micro-supercapacitor is illustrated in Figure 6 and described below. First, LSG interdigitated

microelectrodes were printed directly on a GO film supported on a gold coated polyimide (or a polyethylene terephthalate) substrate using a consumer grade DVD burner (23). Second, MnO_2 nanoflowers were grown on one set of the interdigitated electrodes using the electro-deposition setup described above. The applied current was normalized to the active LSG deposition area at a current density of 250 $\mu A/cm^2$ and the mass loading was controlled by adjusting the deposition time. Likewise, symmetric micro-supercapacitors based on LSG/MnO_2 as both the positive and the negative electrodes were prepared as well. Here, the fabrication process is the same except that the two sides (instead of one side) of the bare interdigitated LSG electrodes were connected together using copper tape and used as the working electrode during electro-deposition.

Characterization and measurements. The morphology and microstructure of the different electrodes were investigated by means of field emission scanning electron microscopy (JEOL 6700) equipped with energy dispersive spectroscopy (EDS) and optical microscopy (Zeiss Axiotech 100). XPS analysis was performed using a Kratos Axis Ultra DLD spectrometer. The thicknesses of the different components of the device were measured using cross-sectional scanning electron microscopy and a Dektak 6 profilometer. The electrochemical performances of the LSG-MSC supercapacitors were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge tests and electrochemical impedance spectroscopy (EIS). CV testing was performed on a VersaSTAT3 electrochemical workstation (Princeton Applied Research, USA). Charge/discharge and EIS measurements were recorded on a VMP3 workstation (Bio-Logic Inc., Knoxville, TN) equipped with a 10 A current booster. EIS experiments were carried out over a frequency range of 1 MHz to 10 mHz with an amplitude of 10 mV at open-circuit potential. Calculations of the specific capacitance and the energy and power densities are discussed in detail in the following sections.

Calculations. The capacitances of the supercapacitors were calculated based on both cyclic voltammetry (CV) profiles and galvanostatic charge/discharge curves (CC). For the CV technique, the capacitance was calculated by integrating the discharge current (i) vs. potential (E) plots using the following equation:

$$C_{device} = \frac{\int i dV}{v \times \Delta E} \qquad (1)$$

where v is the scan rate (V/s) and ΔE is the operating potential window.

The capacitance was also calculated from the charge/discharge (CC) curves at different current densities using the formula:

$$C_{device} = \frac{i_{app}}{dE/dt} \qquad (2)$$

where i_{app} is the current applied (in amps, A), and dV/dt is the slope of the discharge curve (in volts per second, V/s). Specific capacitances were calculated based on the area and the volume of the device stack according to the following equations:

$$Areal\ capacitance\ (C_A) = \frac{C_{device}}{A} \qquad (3)$$

$$Volumetric\ stack\ capacitance\ (C_v) = \frac{C_{device}}{V} \qquad (4)$$

where A and V refer to the area (cm^2) and the volume (cm^3) of the device, respectively. The stack capacitances (F/cm^3) were calculated taking into account the volume of the device stack. This includes the active material, the current collector and the separator with electrolyte.

The energy density of each device was obtained from the formula given in Equation (5):

$$E = \frac{1000}{2 \times 3600} C_v \Delta E^2 \qquad (5)$$

where E is the energy density in Wh/l, C_v is the volumetric stack capacitance obtained from galvanostatic charge/discharge curves using Equation (3) in F/cm^3 and ΔE is the operating voltage window in volts.

The power density of each device was calculated using the equation:

$$P = \frac{E}{t} \qquad (6)$$

where P is the power density in W/l and t is the discharge time in hours.

Since the majority of volumetric capacitances reported in the literature are based on the volume of the active material only, we did the same calculations for the purpose of comparison using the following equations:

Volumetric capacitance of the device,

$$C_{v(device)} = \frac{C_{device}}{V} \qquad (7)$$

where V is the volume of the active material on both electrodes

Volumetric capacitance per electrode,

$$C_{v(electrode)} = 4 \times C_{v(device)} \qquad (8)$$

The specific capacitance contributed by MnO_2 alone was calculated by subtracting the charge of the bare LSG framework according to the equation $C_{s,MnO2} = (Q_{LSG/MnO2} - Q_{LSG})/(\Delta V \times m_{MnO2})$ [31]. Here Q is the voltammetric charge, ΔV is the operating potential window and m is the mass.

Asymmetric cells. In order to achieve optimal performance with asymmetric supercapacitors, there should be a charge balance between the positive and negative electrodes. The charge stored by each electrode depends on its volumetric capacitance ($C_{v(electrode)}$), volume of the electrode (V), and the potential window in which the material operates (ΔE).

$$q = C_{v(electrode)} \times V \times \Delta E \qquad (9)$$

To attain the charge balance, the following condition must be satisfied

$$q_+ = q_- \quad (10)$$

$$\frac{V_+}{V_-} = \frac{C_{v(electrode)-} \times \Delta E_-}{C_{v(electrode)+} \times \Delta E_+} \quad (11)$$

The charge balance was achieved by adjusting the thickness of the positive and negative electrodes.

Comparison with commercial energy storage systems. In order to put the LSG/MnO_2 hybrid supercapacitors and micro-supercapacitors into perspective, we tested the performance of a wide range of commercially available energy storage systems for comparison. This includes activated carbon supercapacitors, a pseudo-capacitor (2.6 V, 35 mF), a battery-supercapacitor hybrid (lithium ion capacitor) (2.3 V, 220 F), an aluminum electrolytic capacitor (3 V, 300 μF) and a lithium thin-film battery (4 V/ 500 μAh). Activated carbon supercapacitors of varying sizes were tested: small size (2.7 V, 0.05 F), medium size (2.7 V, 10 F) and large size (2.7 V, 350 F). The activated carbon large cell (2.7 V, 350 F) was tested at a lower current density of 160 mA/cm^3 due to a limitation in our measuring equipment that provides 10 A maximum current. All the devices were characterized under the same dynamic conditions as the LSG/MnO_2 hybrid supercapacitors and micro-supercapacitors. Data for the Li battery are reproduced from ref. [22].

XPS analysis. XPS was successfully used for better understanding of the chemical composition and the oxidation state of Mn in the LSG/MnO_2 electrodes. The Mn 2p and Mn 3s spectra are presented in Fig. 3 F-G. The peaks of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are located at 642.1 and 653.9 eV, respectively, with a spin energy separation of 11.6 eV, which is in good agreement with data for Mn 2p states previously reported [18-24 in the main manuscript]. Toupin *et al.* showed that the peak separation of the Mn 3s doublet is related to the oxidation state of Mn in manganese oxides, where reference samples of MnO, Mn_3O_4, Mn_2O_3 and MnO_2 showed a separation of 5.79, 5.50, 5.41 and 4.78 eV,

respectively [32]. The as-prepared LSG/MnO_2 showed a separation energy of 4.8 eV for the Mn 3s doublet (Fig. 3G), suggesting that the oxide is MnO_2 which was further confirmed from the O 1s spectrum.

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