High-Performance Nanostructured Supercapacitors on a Sponge

Wei Chen,‡ R. B. Rakhi,‡ Liangbing Hu,‡ Xing Xie,§ Yi Cui,‡ and H. N. Alshareef*‡,†

‡Materials Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia 23955-6900
†Department of Materials Science and Engineering and §Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305, United States

ABSTRACT: A simple and scalable method has been developed to fabricate nanostructured MnO₂—carbon nanotube (CNT)—sponge hybrid electrodes. A novel supercapacitor, henceforth referred to as “sponge supercapacitor”, has been fabricated using these hybrid electrodes with remarkable performance. A specific capacitance of 1230 F/g (based on the mass of MnO₂) can be reached. Capacitors based on CNT—sponge substrates (without MnO₂) can be operated even under a high scan rate of 200 V/s, and they exhibit outstanding cycle performance with only 2% degradation after 100000 cycles under a scan rate of 10 V/s. The MnO₂—CNT—sponge supercapacitors show only 4% of degradation after 100000 cycles at a charge—discharge specific current of 5 A/g. The specific power and energy of the MnO₂—CNT—sponge supercapacitors are high with values of 63 kW/kg and 31 Wh/kg, respectively. The attractive performances exhibited by these sponge supercapacitors make them potentially promising candidates for future energy storage systems.

KEYWORDS: Sponge supercapacitor, energy storage, specific capacitance, specific power, MnO₂, carbon nanotubes

Supercapacitors, also known as ultracapacitors, are promising energy storage devices that bridge the gap between batteries and conventional capacitors. Supercapacitors can provide higher energy density than conventional capacitors and much higher power density than batteries.1−4 They exhibit a promising set of features such as high power density, fast rates of charge—discharge, reliable cycling life, and safe operation.1−5 Supercapacitors can be divided into two categories based on the underlying energy storage mechanism.1,3,5 One is electrochemical double layer capacitor (EDLC), where electrical energy is stored by electrostatic accumulation of charges.1 EDLC can provide ultrahigh power and excellent cycle life due to fast and nondegradation process between electrode active materials and electrolyte.2 However, the energy stored in EDLCs is limited by the finite electrical charge separation at the interface of electrode materials and electrolyte, and the availability of surface area.4 Another type of supercapacitor is the so-called pseudocapacitor,1−3,5 in which electrical energy is mainly stored by fast and reversible redox reactions. Because of the Faradaic process underpinning the energy stored in a pseudocapacitor, it has increased energy density but at the cost of power density and cycle life compared to EDLCs. Hybrid supercapacitors combine these two charge storage mechanisms (Faradaic and non-Faradaic), resulting in improved device characteristics.1,2,4,6−11 Typically, carbon based materials are good electrodes for EDLCs,12−16 while transition metal oxides and electrically conducting polymers are good candidates for pseudocapacitors.17−20 Among the different EDLC electrode materials, carbon nanotubes (CNTs) attracted the most attention due to their good conductivity, mechanical flexibility, and stable electrochemical behavior.12,21−24 In comparison, MnO₂ is the most thoroughly investigated transition metal oxide for pseudocapacitors due to its high theoretical specific capacitance (1370 F/g).25 It, relatively low cost, and environmental friendliness.17,26 However, the theoretical capacitance of MnO₂ has rarely been achieved in experiment,25 mainly due to its poor electrical conductivity (10−5−10−6 S/cm). In order to get high specific capacitance from MnO₂, many studies have been conducted, most of which are based on incorporating MnO₂ with conductive materials and forming hybrid electrode structures.7,8,26−28 Several examples of MnO₂ based hybrid electrodes have been recently demonstrated. Hou et al. synthesized MnO₂/CNT/conducting polymer ternary electrodes with a specific capacitance of 427 F/g (based on three-electrode setup).29 Bao et al. demonstrated flexible supercapacitors using Zn₃SnO₄/MnO₂ core/shell nanocable coated on carbon microfiber with a specific capacitance of 642.4 F/g (based on three-electrode setup).30

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Very recently, Lang et al. developed a supercapacitor based on nanoporous gold and MnO$_2$ with a high specific capacitance of 1145 F/g (based on a two-electrode setup), which is close to the theoretical value.$^{31}$ However, these fabrication processes are either too complicated or limited in scalability. Previously, we have exploited paper and textile as substrates to fabricate supercapacitors since they provide a highly porous structure for the fast access of ions to electrolytes.$^{32-35}$ Different from the paper and textile in the previous work, here we exploited sponge as the substrate for supercapacitors.

Sponges, with a hierarchical macroporous nature, have been widely used in our daily life as cleaning tools and can be found everywhere. Sponges are made up of many small cellulose or polyester fibers, which make them highly porous and strong absorbing media with significant internal surface area. A commercial sponge has been employed in our work, which has a high water absorption capacity. A simple experiment showed that it can absorb 45 times more water than its own weight. This indicates the good accessibility and compatibility of sponge to aqueous solutions. Sponges offer novel exciting characteristics different from paper and textile: first, sponge has much more uniform size of macropores. The pore size can be in the range of 100–500 μm. Second, the cellulose or polyester fibers are interconnected virtually free of junctions. Therefore, continuous coating of conducting nanomaterials is much easier since there are no junctions to cross.

We have designed and fabricated high-performance supercapacitors using a simple and scalable method. The fabrication process consisted of four simple steps, as illustrated in Figure 1. A piece of commercially available sponge (pore sizes 100–500 μm) was cleaned by water and acetone several times (Figure 1a). After drying completely in a vacuum oven, the sponge was cut into small ribbons with thickness of 1 mm and area of $1 \times 2$ cm$^2$. The sponge ribbons were subsequently coated with CNTs using a simple “dipping and drying” process in CNT ink suspension (Figure 1b (for details, see Materials and Methods in Supporting Information)). The next step was to electrodeposit MnO$_2$ nanoparticles on the CNT-coated sponge by galvanostatic electrochemical deposition (Figure 1c). A very small current density ($500 \mu$A/cm$^2$) was required to obtain the desired nanostructure of MnO$_2$. To study the dependence of supercapacitor performance on MnO$_2$ deposition time, we deposited MnO$_2$ on CNT-sponge for different times: ranging from 3 to 40 min. The deposition area of each sample was $1 \times 1$ cm$^2$. In the last step (Figure 1d), two identical MnO$_2$–CNT–sponges were sandwiched with a piece of polymer separator dipped in 1 M Na$_2$SO$_4$ electrolyte inserted in between and sealed in a coin cell to complete the symmetrical two electrode assembly (for details, see Supporting Information).

The weight of a clean $1 \times 2$ cm$^2$ sponge is about 10 mg, which is much lighter than a rigid metal and other flexible substrates with the same area.$^{36-38}$ Due to the mechanical flexibility of CNTs and strong van der Waals interactions between the macroporous sponge cellulose and CNTs, the CNTs can be easily coated onto the skeleton of a sponge, rendering the insulating sponge highly conductive by a simple dipping and drying process.$^{35}$ The mass of CNT on the CNT-sponge is $\sim 0.24$ mg/cm$^2$ after two times of dipping and drying. The CNT–sponge has a sheet resistance of 1 Ω/square, measured by four points probe technique. After conformal coating of CNTs onto the skeleton of the sponge, it still maintained a hierarchical macroporous nature where its intricate assembly of pores remained open to allow the flow of electrolyte (Supporting Figure 1S-a). The CNTs coated on the sponge have formed a thin layer of CNT network wrapped around the skeleton of sponge (Supporting Figure 1S-b,c). The amount of CNTs coating the sponge can be readily controlled by the dipping time and ink concentration. In this work, we optimized the dipping time to maximize the amount of CNTs coated on the sponge without blocking its pores. Undercoating degrades the conductivity of the CNT-sponge electrode while overcoating closes the pores of the sponge and prevents the movement of the electrolyte ions. The mechanical resilience of the CNT–sponge skeleton was tested by folding, twisting, and stretching it repeatedly (as shown in Supporting Figure 1S-d,e,f). After all the mechanical tests, the CNT–sponge always reverted to its original shape without any permanent deformation.

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**Figure 1.** Fabrication process of MnO$_2$–CNT–sponge supercapacitors: (a) a piece of sponge is cleaned and cut into small ribbons; (b) CNTs are coated onto the skeleton of the sponge by a “dipping and drying” method; (c) nanostructured MnO$_2$ is electrodeposited onto the conductive CNT–sponge skeleton; (d) two pieces of MnO$_2$–CNT–sponge electrodes were assembled into coin cell to form a MnO$_2$–CNT–sponge supercapacitor.
Scanning electron microscopy (SEM) images of MnO$_2$--CNT--sponge showed clearly the three-dimensional (3D) hierarchical macroporous open-pore structure (Figure 2a (Supporting Figure 2S-a)). Flower-like MnO$_2$ nanoparticles were uniformly deposited onto the conductive CNT--sponge skeleton, even at the edges (Figure 2b,c (Supporting Figure 2S-b,c)). This further confirms that CNTs have been conformably coated on the sponge. Figure 2a also shows an exciting point: the backbone of sponge is free of junctions and promotes the continuous coating of CNTs to form excellent conducting pathways in the whole structure. After deposition of MnO$_2$, the highly porous nanostructure remained, which is good for the fast transportation of electrons and ions in the supercapacitor devices. The deposition mass of MnO$_2$ can be well controlled by adjusting the deposition time (Supporting Figure 3S). We found that the surface of the CNT--sponge can be fully covered by MnO$_2$ after 10 min of electrodeposition (Supporting Figure 3S-c). Increasing the deposition time will increase the mass loading and the thickness of MnO$_2$ (as shown in the Supporting Information Figure 3S). If the electrodeposition is run for 1 h, a very thick film of MnO$_2$ with some cracks can be observed due to the large thickness (Supporting Figure 3S-f). Transmission electron microscopy (TEM) images revealed that the nanostructure of MnO$_2$ is highly porous and includes many small nanoplates (Figure 2d (Supporting Figure 2S-d)). The average pore size of the MnO$_2$ is around 3.2 nm, and it has a BET specific surface area of 174 m$^2$/g (Supporting Figure 4S). An HRTEM image together with selected area electron diffraction (SAED) pattern demonstrated that the deposited MnO$_2$ are polycrystalline (Figure 2e and inset (Supporting Figure 2S-e)). We further confirmed that the polycrystalline MnO$_2$ nanoparticles belong to ε-MnO$_2$ by X-ray diffraction (XRD) (JCPDS 00-030-0820) (Figure 2f). The flower-like MnO$_2$ nanoparticles on macroporous CNT--sponge essentially form a so-called double porous nanostructure. This unique structure provides outstanding performance for the intercalation/deintercalation of electrolyte cations into electrode materials, and we therefore expect a high performance supercapacitor.

The electrochemical performance of CNT--sponge substrate was tested using a two-electrode coin cell configuration. Two pieces of symmetrical CNT--sponge, one piece of separator, and 1 M Na$_2$SO$_4$ have been used as electrodes, separator, and electrolyte, respectively. All measurements have been conducted at room temperature. As shown in panels a and b of Figure 3, the CNT--sponge devices (without MnO$_2$ deposition) can be operated over a wide range of scan rates: from 0.001 up to 200 V/s. The cyclic voltammograms retain the rectangular shape (which is characteristic of the ideal electrochemical double layer capacitive behavior) even at a high scan rate of 20 V/s. As expected, the currents increase with the applied scan rates, but surprisingly the CNT--sponge devices operate at the highest reported scan rate for aqueous electrolyte supercapacitors. We can therefore conclude that ultrahigh power can be obtained from this kind of device. Another good feature of the CNT--sponge device is its good electrochemical behavior even at an extremely high scan rate of 200 V/s, which is comparable to microsupercapacitors built on rigid silicon substrates. Furthermore, a linear dependence of the discharge current on the scan rate up to 8 V/s can be observed from Figure 3c. The deviation of the linear dependence after 8 V/s is due to the diffusion.
The discharge currents are calculated from the discharge scan with an average over the whole voltage range at specific scan rates. A mean areal capacitance of 0.36 mF/cm² can be obtained from the slope of Figure 3c, which is comparable to the value of carbon materials based microsupercapacitors. A maximal value of 0.9 mF/cm² can also be obtained at a scan rate of 1 mV/s, but this value can be improved if more CNTs have been coated on the sponge.

Figure 3d illustrates the charge–discharge behavior of the CNT–sponge device. The figure shows ultrafast charge–discharge rate and linear dependence on voltage and time, with very small voltage drop at a specific current of 10 A/g. These results indicate that the CNT–sponge substrates used in the present work exhibit excellent supercapacitor performance. More importantly, these results coupled with other promising features of the CNT–sponge (such as ease of fabrication, low cost, lightweight and flexibility) make it a highly promising energy storage substrate.

Figure 4e shows the MnO₂–CNT–sponge electrodes prepared by electrochemical deposition of MnO₂ onto conductive CNT–sponge. The amount of MnO₂ was controlled by the deposition time. Here, we varied the deposition time from 3 to 40 min. It was observed that as the deposition time increased, the mass loading of MnO₂ increased accordingly. This can be observed from the increased darkness of the sponge as shown in Figure 4b. The first ribbon on the left in Figure 4b is a bare sponge, and the second one from the left is a CNT–sponge without MnO₂ on it. The remaining samples from left to right are MnO₂–CNT–sponge with deposition time from 3 to 40 min. The color of the bottom part of the CNT–sponge becomes darker with increased electrodeposition time, which means more MnO₂ has been deposited on the sponge. This can be further confirmed by plotting the change of MnO₂ content and MnO₂ mass loading versus deposition time (Figure 4a). As can be seen from Figure 4a, the MnO₂ content (the weight percentage of MnO₂ in MnO₂–CNT composite) and its mass loading increased with the deposition time. Each data point in Figure 4a is an average value of at least 10 samples. At low deposition time, e.g., 10 min, the MnO₂ mass loading is around 0.1 mg/cm² and its content in the MnO₂–CNT composite is nearly 30% by weight. These values are higher than the values obtained from rigid metal substrates such as platinum at the same deposition time due to the large surface area of the sponge. When the electrodeposition time increased to 40 min, the mass loading of MnO₂ increased to 0.5 mg/cm², which is more than twice the CNT loading on the sponge, and the corresponding MnO₂ content in the MnO₂–CNT composite is as high as 67% by weight. For long deposition times, e.g., 20 h, the mass loading of MnO₂ can go up to 12.8 mg/cm², which is twice the weight of the CNT–sponge itself.

Figure 3. Electrochemical behaviors of CNT–sponge substrates: (a and b) cyclic voltammetry scan from 0.001 to 10 V/s and from 20 to 200 V/s, respectively; (c) discharge currents as a function of scan rates (linear relation is obtained up to scan rate of 8 V/s); (d) galvanostatic charge–discharge curves at a specific current of 10 A/g. The mass of CNT on the CNT-sponge substrate is ∼0.24 mg/cm².
To reveal the good adhesion between MnO$_2$ and CNT–sponge, a simple Scotch tape adhesion test was performed comparing the MnO$_2$/CNT–sponge and MnO$_2$/platinum electrodes. It can be seen clearly from Figure 4c that superior adhesion performance is observed for the MnO$_2$/CNT–sponge: no peeling was observed in the case of MnO$_2$/CNT–sponge (Figure 4c), while significant peeling was observed in the case of the rigid Pt foil (Figure 4d). Another result that demonstrates the superior electrochemical performance of the MnO$_2$/CNT–sponge electrodes is comparing its cyclic voltammetry behavior to the flat MnO$_2$–Pt substrate. A three-electrode configuration has been setup to test the electrochemical performances by cyclic voltammogram (for details, see Supporting Information). At scan rate of 50 mV/s (Figure 4f), the electrochemical performance of MnO$_2$/CNT–sponge outperforms that of MnO$_2$–Pt electrode in terms of wider voltage range and higher capacitance. At a 5 min electrodeposition of MnO$_2$, a very high specific capacitance of 1230 F/g can be achieved from MnO$_2$/CNT–sponge electrode at scan rate of 1 mV/s. However, the value is just 155 F/g for MnO$_2$–Pt electrode under the same conditions (Figure 4g). This controlled experiment further confirms the outstanding electrochemical performance of MnO$_2$/CNT–sponge electrode.

To completely investigate the electrochemical performances of MnO$_2$/CNT–sponge supercapacitors, a typical two-electrode configuration has been employed in this work. The MnO$_2$/CNT–sponge serves as electrode as well as current collector, and the integrated binder-free structure provides highly porous and conductive channels for the full access of electrolyte ions to the active electrode material in supercapacitors. As shown in panels a and b of Figure 5, the full cell has been studied by cyclic voltammograms over a wide range of scan rates: from 0.001 to 10 V/s. Take the 5 min MnO$_2$ deposition sample as an example. The cyclic voltammogram (CV) shapes are almost rectangular at scan rates below 2 V/s and remain quasi-rectangular at a scan rate up to 10 V/s (Figure 5b), indicating the excellent charge storage characteristics and ultrafast response of the electrodes. The high scan rate of 10 V/s is 1 to 2 orders of magnitude higher than the rate used in most of the literature for the MnO$_2$/CNT composite electrodes with aqueous electrolyte. The voltage versus time profiles were obtained by galvanostatic charge–discharge measurements (Figure 5c). The device can be steadily operated over a wide range of applied specific current, from 1 to 100 A/g. The internal resistances (including the electrical resistances of electrodes, the ions diffusion resistances, and the interfacial resistance between the electrode and electrolyte) derived from the voltage drop are
consistent with the values calculated from impedance electrochemical spectroscopy (Supporting Figure 5S). The cyclic voltammetry responses of different samples under different deposition times have been demonstrated in panels d and e of Figure 5, at specific scan rates of 20 and 200 mV/s, respectively. The corresponding current increases with MnO₂ content on the electrodes for both scan rates, suggesting that more materials contributed to charge storage. When the scan rate changed from 20 to 200 mV/s, the CV shapes remained nearly rectangular, with only a few deviations for samples with high mass loading. This clearly shows the excellent electrochemical performance of the MnO₂-CNT-sponge supercapacitors. The specific capacitances with respect to the mass of MnO₂ have been derived from CVs and plotted in Figure 5f, which are comparable with the values calculated from galvanostatic charge-discharge curves. A specific capacitance of 1000 F/g can be obtained based on the mass of MnO₂ at scan rate of 1 mV/s. The specific capacitances of MnO₂-CNT-sponge supercapacitors are competitive with literature values. The specific capacitance decreases with the scan rates and MnO₂ deposition times but remains constant at scan rates higher than 100 mV/s. The measured specific capacitance depends strongly on scan rate for low mass loading devices but depends weakly on scan rate for high mass loading devices. For example, the specific capacitance decreased from 1000 F/g at 1 mV/s to 581 F/g at 100 mV/s for the 3 min electrodeposition device. In comparison, it decreased from 444 F/g at 1 mV/s to 295 F/g at 100 mV/s for the 10 min electrodeposition device. For higher mass loading devices, such as 30 and 40 min MnO₂ depositions, negligible change in specific capacitance was observed, especially at high scan rates. This is mainly due to the limited conductivity of high mass loading samples and the limited utilization of MnO₂ at high scan rates. At low mass loading of MnO₂, the highly conductive double porous electrodes provide good opportunity for electron transportation and ions accessibility, maximizing the utilization of MnO₂ materials.

Looking into the charge storage mechanisms of MnO₂-CNT-sponge supercapacitors, a possible electrochemical reaction can be proposed as follows

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\text{MnO}_2 + x\text{H}^+ + y\text{Na}^+ + (x + y)e^- \leftrightarrow \text{MnOOH}_x\text{Na}_y
\]

The energy storage contributions come from both surface adsorption/desorption of electrolyte cations (Na⁺) to the surface of CNTs and MnO₂, and the fast, reversible redox reactions by means of intercalation/extraction of protons into/out of MnO₂. The conductive double porous structure facilitates the adsorption/desorption of Na⁺ and the transportation of electrons and protons, allowing full access of the electrolyte to electrode materials and maximizing the utilization of MnO₂. Therefore, the cyclic voltammograms exhibit the ideal rectangular shapes and a specific capacitance of 1000 F/g can be obtained based on the mass of MnO₂.

Electrochemical impedance spectroscopy (EIS) and long time cycling stability are two important parameters to determine the performances of supercapacitors. Figure 6a and inset show the Nyquist plots in the frequency range from 100 kHz to 0.01 Hz, which can be represented by the equivalent circuit and the corresponding model for ideal supercapacitors, as shown in Figure 6b (refs 1, 7, and 30). In the equivalent circuit, a solution resistance (\(R_S\)) connects in series with a constant phase element (CPE), and the CPE connects in parallel with the charge transfer
resistance \( (R_{CT}) \) and pseudocapacitance \( (C_p) \). The solution resistance refers to the resistance from the electrolyte, the CPE accounts for the double-layer capacitance, and the charge transfer resistance (also called Faraday resistance) corresponds to the total resistance at the interface between the electrode and the electrolyte.44 Experimental results show that \( R_S \) is insensitive to the surface condition of the electrode, and it is consistent with a value of around 1.5 \( \Omega \) for all our devices. However, \( R_{CT} \) increases with the mass loading of \( \text{MnO}_2 \) on the surface of the CNT—sponge, from 4.5 \( \Omega \) at 3 min \( \text{MnO}_2 \) electrodeposition to 28 \( \Omega \) at 40 min deposition (Figure 6a). Typically, the Nyquist plot can be divided by the so-called knee frequency into a high frequency semicircle and a low frequency vertical line,44 as schematically illustrated in Figure 6b. The semicircle intersection with the abscissa depends on the internal resistance, and the vertical line implies good capacitive behaviors of supercapacitors. The internal resistances (including \( R_S \), \( R_{CT} \) and other resistances) of all samples are summarized and plotted in Supporting Figure 5S. These values are consistent with those derived from the voltage drop of charge—discharge curves. This result clearly indicates that the internal resistance increases with the \( \text{MnO}_2 \) deposition time due to increased mass loading of semiconducting \( \text{MnO}_2 \), making the \( \text{MnO}_2—\text{CNT}—\text{sponge electrode less conductive. A long time charge—discharge cycling up to 100000 cycles has been performed on CNT—sponge devices using a scan rate of 10 V/s. The results, shown in Figure 6c, indicate that 98% of the initial capacitance is retained. In comparison, the cycling stability of \( \text{MnO}_2—\text{CNT}—\text{sponge supercapacitors was also investigated up to 10000 charge—discharge cycles using a specific current of 5 A/g. It is seen that 96% of the initial capacitance has been retained after 10000 cycles} \) (Figure 6c inset) for the 40 min \( \text{MnO}_2 \) deposition device. These results demonstrate good stability of both CNT—sponge and \( \text{MnO}_2—\text{CNT}—\text{sponge supercapacitors. Figure 6d shows a Ragone plot of \( \text{MnO}_2—\text{CNT}—\text{sponge supercapacitors. Although it is challenging to compare accurately the performance of all types of supercapacitor due to a large number of variables such as materials mass loadings, charge-discharge rates and testing configurations, the rough comparison can still be made. The Ragone plot shows that the specific energy and specific power values of our sponge supercapacitors are very competitive compared to the ones reported in the literature,}^{22,27,30,31,43,45,46} \) with maximum specific energy of 31 Wh/kg and specific power of 63 kW/kg. The CNT—sponge device showed ultrahigh specific power of 105 kW/kg, although the specific energy is low. All the specific energy and power values were calculated from the galvanostatic charge—discharge curves. These values demonstrate the

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**Figure 6.** Nyquist plot, equivalent circuit model, long time cycling, and Ragone plot of \( \text{MnO}_2—\text{CNT}—\text{sponge supercapacitors:} \) (a) Nyquist plot of supercapacitor devices with different \( \text{MnO}_2 \) deposition times, ranging from 0 to 40 min; (b) equivalent circuit model of the device; (c) capacity retention vs cycle number for CNT—sponge device up to 100000 cycles at a high scan rate of 10 V/s and 40 min \( \text{MnO}_2—\text{CNT}—\text{sponge supercapacitors under 10000 cycles at a specific current of 5 A/g, respectively;)} \) (d) Ragone plot of \( \text{MnO}_2—\text{CNT}—\text{sponge supercapacitors under different mass loadings of \( \text{MnO}_2 \).} \)
outstanding capability of CNT–sponge and MnO$_2$–CNT–sponge supercapacitors as high-power and high-energy storage systems.

In summary, novel sponge supercapacitors have been fabricated using a simple method while providing remarkable performance. The macroporous nature of the sponge along with the porous nature of the electrodeposited MnO$_2$ nanoparticles provided a double porous electrode structure giving good conductivity and full accessibility of electrolyte to MnO$_2$, improving the performances of MnO$_2$–CNT–sponge supercapacitors dramatically. The MnO$_2$–CNT–sponge supercapacitor exhibits high specific capacitance, ultrafast charge–discharge rate, excellent cycling stability, and good energy and power density, making it a promising electrode for future energy storage systems.

**ASSOCIATED CONTENT**

Supporting Information. Material and Methods and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: husam.alshareef@kaust.edu.sa*

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