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Supporting Information

Editable Supercapacitor with Customizable Stretchability Based on Mechanically Strengthened Ultralong MnO₂ Nanowire Composites

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Keywords: Editable supercapacitors; stretchable devices; programmability; manganese dioxide nanowires

1. Experiment Section

2. Supporting Notes

2.1 The formation process of ultralong MnO₂ nanowires through stirring hydrothermal method

2.2 Charge storage reactions of MnO₂ electrodes in LiCl electrolytes

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Figure S2 SEM images of MnO₂ nanostructures synthesized in this study with different stirring conditions: (a) 0 rpm for 24 h, (b) 500 rpm for 3 h, (c) 500 rpm for 6 h, (d) 500 rpm for 12 h, (e) 500 rpm for 18 h, and (f) 500 rpm for 24 h.

Figure S3 TEM images of MnO₂ nanostructures synthesized in this study with different stirring conditions: (a) 500 rpm for 0.5 h, (b) 500 rpm for 1 h, (c) high resolution image for 500 rpm for 1 h, (d) 500 rpm for 3 h, (e) 500 rpm for 6 h, (f) 500 rpm for 24 h. (g) high resolution image of 0 rpm for 24h and (h) the SAED pattern of MnO₂ nanoflowers.

Figure S4 (a) XRD patterns of MnO₂ materials obtained from tradition hydrothermal and stirring hydrothermal method (24 h). (b) XRD patterns of MnO₂ samples obtained from stirring hydrothermal (500 rpm) under different reaction time.

Figure S5 (a) Photograph of MNW/CNT and MNF/CNT composite with different weigh ration of CNT. The number suffixed to MNW and MNF represents weight percent of MNW or MNF in the composite film, respectively. MNF100, MNF90, and MNF80 cannot be peeled off from the filter paper due to poor mechanical integrity. MNF70 is barely able to form

freestanding film, as illustrated by the incomplete film. Other films are easily detached from the filter paper. (b) The break of MNW100 film under a slight bending. Stress-strain curves of (c) MNW/CNT and (d) MNF/CNT composite films. (e) Comparison of ductility of MNW/CNT and MNF/CNT composite films with varying CNT content.

Figure S6 Electrical conductivity of MNW/CNT and MNF/CNT composite films with the increasing CNT weight ratio.

Figure S7 (a) Cyclic voltammograms of MNW/CNT composite films with different CNT content. The scanning rate of CV is 50 mV s^{-1} . (b) Specific capacitance measured from cyclic voltammetry curves at increasing scanning rate for MNW/CNT films (0.6 mg cm^{-2}) with different content of CNT.

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Figure S15 Dependence of strain on L_c with thickness of 1 mm (inserted, the schematic of a basic unit of the kirigami pattern on stretchable supercapacitor, where the L_c is the cut length, x and y is the space length in transverse and axial direction). (b) Stress-strains curve for the paper-cut supercapacitors with linear patterns

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times to 435 mF cm^{-2} . (b) The increase of the specific areal capacitance of editable supercapacitors by vertical stacking in parallel. The resulted editable supercapacitor with five stacking units can increase the specific areal capacitance to 1090 mF cm^{-2} under tensile strain of 400% at a charging-discharging current density of 1.6 mA cm^{-2} .

Figure S20 Digital images of editable supercapacitors tailed into (a) honeycomb-like structure, (b) supercapacitor pyramid and (c) stereoscopic Chinese word ‘spring’ under unfold and fold condition. (d) The pop-up spring-like supercapacitor strips pasted on two sides of arms to power a red LED.

1. Experimental Section

Preparation of MnO₂ Nanomaterials (MNFs and MNWs): MnO₂ nanoflowers (MNFs) and nanowires (MNWs) are respectively synthesized through hydrothermal method without or with magnetic stirring, as shown in Figure S1. In a typical synthesis process, a 15 ml aqueous mixture solution containing 0.4 mM KMnO₄ and 0.4 mM NH₄Cl was firstly transferred into a 20 ml Teflon-lined autoclave, and then underwent reaction at 150 °C for 24 h in an oil bath without magnetic stirring for MNF synthesis or with magnetic stirring at 500 rpm for MNW synthesis. MNFs with the length of 1~2 μm and 20~30 μm respectively synthesized at the stirring speed of 300 rpm and 400 rpm by the stirring hydrothermal method. The as-synthesized MnO₂ materials were collected and washed with deionized water (DI water) for five times using a centrifuge to remove residues. Washed MNFs and MNWs were re-dispersed in ethanol, poured into a Petri dish and dried at 100 °C for 12 h to evaporate solvent. Dried films were crushed into powders and stored for later use.

Fabrication of Flexible MnO₂ Composite Films: MnO₂ nanomaterials/single-walled carbon nanotube (CNT) composite electrodes were produced via vacuum filtration for later test. In brief, CNT powders (Bu-202, BuckyUSA) was firstly treated with 1M HNO₃ aqueous solution to remove the metallic impurities, followed by filtration with DI water for five times. Then, weighed amount of MNFs or MNWs and aqueous mixture solution with 1 mg mL⁻¹ CNT and 2 mg mL⁻¹ sodium dodecyl benzene sulfonate (SDBS) mixtures were transferred into ethanol to form 40 mL mixture solutions. The mixture solutions were then operated under stirred magnetic stirring at 1000 rpm for 12 h. After 1 h bath sonication, the other 1 h probe-type sonication was used to obtain a homogenous mixture solution. The mixture solutions were further vacuum-filtrated on a polyvinylidene fluoride (PVDF) filter membranes (0.2 μm) and was then thoroughly rinsed with DI water to remove the residual SDBS. The as-prepared composite film electrodes were finally peeled off from the PVDF filter membrane and vacuum-dried at 80 °C for 12 h. For PPy(polypyrrole)-modified MNW/CNT composite

electrode, a constant potential of 0.8 V was applied for the anodic electropolymerization of PPy on the MnO₂/CNT composite electrode in a non-stirred N₂-saturated aqueous solution that contained 10 mM 9,10-anthraquinone-2-sulfonic acid (AQS) and 0.12 M pyrrole. The deposition of PPy was controlled by varying the total charge passed to these working electrodes. The as-received PPy-modified MNW/CNT electrode was washed by DI water for several times and vacuum-dried at 80 °C for 12 h.

Preparation of Gel Electrolyte: For the preparation of PVA/LiCl gel electrolyte, 8 ml of DI water was added to 1 g of PVA powder (99% hydrolyzed, M_w =86000~98000, Aldrich®), and the mixture was stirred vigorously at 90 °C. Meanwhile, 1 g of LiCl (≥ 99.0%, Sigma-Aldrich) was dissolved in 2 ml of DI water. When the PVA aqueous solution turned clear, LiCl solution was dropped into the PVA aqueous, and stirred for another 2 h for complete solvation and homogeneous mixing.

Assembly of Flexible and Stretchable Supercapacitors: The as-obtained reinforced electrode was noted as MNF/CNT-NCF or MNW/CNT-NCF electrode, and the part to connect current collector was well-protected by a designed double-sided conductive tap to avoid the coverage of nanocellulose fibers in this area. After that, the part of electrode in the nanocellulose films was soaked into the PVA gel electrolyte. Then two electrodes were overlapped with each other to prepare a symmetric supercapacitor and the PVA gel electrolyte was pasted one more times on the overlapped area. The as-prepared symmetric supercapacitors were left on a vacuum chamber to release the gas in the electrolyte. Finally, the as-fabricated SCs were left on the fume hood overnight (about 12h) to wait for the solidification of the gel electrolyte. For stretchable supercapacitor, a flexible supercapacitor was firstly fabricated. After drying flexible supercapacitors in oven at 40 °C for 1 h, a scissor was directly used to cut the as-prepared flexible supercapacitor in the overlapped part, creating the various shapes and structures.

Material and Mechanical Characterization: Crystal structures of MNWs and MNFs were investigated using thin film XRD (LabX XRD-6000, Shimadzu) with Cu K α radiation. Thin film samples were prepared by spreading ethanol dispersion of nanoparticles dropwise on glass slides with concurrent evaporation of ethanol. Surface elemental and oxidation state of Mn species analysis was obtained by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 220I-XL system equipped with a monochromatic Al K α (1486.6 eV) source and a concentric hemispherical energy analyzer. All samples were subjected to drying at 120°C for 2 h to evaporate trace water before measurement. Microscopic morphologies of various nanoparticles and composites were recorded using SEM (JEOL JSM-6340F or 7600) and TEM (JEOL 2010 HR or 2010 UHR). Tensile tests of bare MnO₂/CNT films were conducted using Mechanical Tester MTS Model C42. Electrical conductivity of vacuum-filtered films was measured using a four-probe resistivity measurement system. Three points were measured for each film of a specific composition.

Electrochemical Characterization: Cyclic Voltammetry (CV), Galvanostatic charging-discharging (GCD) and electrochemical impedance spectroscopy (EIS) tests were conducted to test the electrochemical performance of composite electrodes and the supercapacitors. The CHI 660d potentiostat (Shanghai Chenhua) were used to measure the electrochemical performance of the as-prepared single MnO₂ composite electrodes and the corresponding symmetric supercapacitors. Electrochemical performance of MnO₂/CNT electrode was characterized in aqueous electrolyte of 5 M LiCl using electrochemical workstation in a three-electrode configuration, where Pt is counter electrode, Ag/AgCl is reference electrode and vacuum-filtered film as working electrode. For the electrochemical characterization of symmetric supercapacitors, the same equipment was used. The two electrodes in a supercapacitor were connected as working electrode and counter/reference electrode, respectively. The current outputs of the integrated devices with or without integrated stretching (Figure 5) were recorded by Keithley 4200A-SCS.

Specific mass capacitances of composite electrodes were calculated based on CV (C_{A-CV} , mF g⁻¹) and GV (C_{A-GV} , mF g⁻¹) curves according to Equation S1-1 and S1-2, respectively. Specific mass capacitances of symmetric supercapacitors were calculated based on GV curves according to Equation S1-3.

$$C_{m-CV} = \frac{\oint I dU}{2vm\Delta U} \quad \text{S1-1}$$

$$C_{m-GV} = \frac{i\Delta t}{m\Delta U} \quad \text{S1-2}$$

$$C_{m-device} = \frac{it}{m_{total}\Delta U} = \frac{it}{m_{total}\Delta U} \quad \text{S1-3}$$

In the above equations, I is response current (A), U is potential (V), v is scanning rate (V s⁻¹), m is electrode mass (mg), m_{total} is the total mass of two electrodes in symmetric supercapacitor (mg), ΔU is potential window (V), i is discharging current (A), and Δt is discharging time (s).

Specific area capacitances (C_{A-GV} , mF cm⁻²) of composite electrodes and devices were calculated based on GV curves according to Equation S1-4. Specific volumetric capacitances (C_{V-GV} , mF cm⁻³) of composite electrodes and devices were calculated based on GV curves according to Equation S1-5.

$$C_{A-GV} = \frac{i\Delta t}{A\Delta U} \quad \text{S1-4}$$

$$C_{V-GV} = \frac{i\Delta t}{V\Delta U} \quad \text{S1-5}$$

In the above equation, I is response current (A), v is scanning rate (V s⁻¹), A is projected area of the electrodes or project area of the overlapped part (cm²) for supercapacitors, V (cm³) is the volume of the supercapacitors, ΔU is potential window (V), i is discharging current (A), and Δt is discharging time (s).

The power density (P_A) and energy density (E_A) of editable supercapacitors were calculated according to Equation S1-6 and S1-7.

$$1 \quad E_A = \frac{C_{A-GV} \times \Delta U^2}{2} \quad \text{S1-6}$$

$$2 \quad P_A = \frac{E_A}{\Delta t} \quad \text{S1-7}$$

3 In the above equation, ΔU is potential window (V), i is discharging current (A), and Δt is
 4 discharging time (s).

5

2. Supporting Notes

2.1 The formation process of ultralong MnO₂ nanowires through stirring hydrothermal method

XRD patterns of all samples (Figure S4) confirm the formation of tetragonal α -MnO₂ phase as all peaks can be matched to standard X-ray diffractogram (JCPDS 44-0141). Planes (110), (220), (211), (420) and (112) are identifiable in all MnO₂ nanoparticles prepared with different conditions. However, (200), (310), (510), (411), (600), (521), and (541) only become visible after 12 h of SH process. From the SEM images shown in Figure S2, nanowires started to dominate after 12 h. Thus the emergence of new peaks in X-ray diffractograms should be related to unidirectional growth of nanowires. As nanowires became longer in size and more abundant in quantity, they tended to grow directionally in contrast to the random orientation of nanoflowers, and the facets parallel to the axial direction of nanowires would produce the diffraction signal.^[5]

Transmission Electron Microscopy (TEM) is further used to investigate the crystal structure as well as the formation process of the MnO₂ nanowires (MNWs) prepared by stirring hydrothermal method, as shown in Figure S4. At the early stage under 0.5 h reaction time, the petal-like moieties with MnO₂ nuclei can be found (Figure S4a), and further prolong the reaction time to 1 h, some short nanowires randomly formed in the petal-like moieties (Figure S4b,c), similar to the morphology of MNFs formed in conventional hydrothermal process with 24 h reaction time (Figure S4g). When increase the reaction time to 3h, the elongated nanowire bundles appeared (Figure S4d). After 6 h reaction, the nanowire bundles structure become longer in length and shrink in diameter under 6 h and the MnO₂ nanowires with high aspect ratio (Figure S4e) was finally formed under 24 h reaction (Figure S4f). These results indicate that the mechanical intervention did not alter morphology of early MnO₂ nuclei and seeds, but stirring may accelerate reactant mass transport.^[6] After the formation of nanoflowers, shear force and altered mass transport condition around MnO₂ nanostructures

introduced by stirring may synergically promote disassembling of nanoflowers into individual nanosheets which then assembled into nanowires. During later growth, nanowires further extended in length along a preferred direction, where the circular flow of reaction solution helped align the nanowires while sheer friction between fluid and nanowires help refine the shape of long wires. Figure S4g and h show the high resolution TEM images and the selected area electron diffraction (SAED) pattern of MNWs prepared by hydrothermal method with or without stirring under 24 h. The inset image of Figure 2c is the SAED pattern of the as-synthesized MNFs. The SAED pattern demonstrates the polycrystalline structure of MNFs which derives from the randomly exposure of crystal face in the MNFs. While for the MNWs, the SAED pattern in Figure 2c index the tetragonal MnO_2 and the nanowires are single crystalline with the growth axis in the $[001]$ direction. The exclusive presence of the $(hk0)$ peaks in XRD test also verifies the most, if not all, nanowires grow along the $[001]$ direction.

2.2 Optimization of weight percent of CNT and mass loading in composite electrode

To optimize the electrochemical performance of nanocomposite electrode, the optimal CNT content in MNW/CNT nanocomposite film (0.6 mg cm^{-2}) was investigated. Figure S8 displays the specific capacitances of MNW/CNT films with CNT content from 10 wt% to 50 wt% measured from cyclic voltammetry (CV) at increasing scanning rates. The optimal CNT content that gives the highest specific capacitance at majority of charging-discharging rates is 30 wt%, below which low electrical conductivity (lower than 150 S cm^{-1} , Figure S6) restricted utilization of all MnO_2 capacitance especially at high rates, and above which the advantages of high pseudo-capacitance from MnO_2 was depressed by the low mass loading. Therefore, MNW/CNT composite films with 70 wt% MnO_2 nanowires and 30 wt% CNTs (noted as MNW70, the number suffix behind ‘MNW’ and ‘MNF’ represents the weight percent of MnO_2 nanoparticles in the composite film) were chosen as the representative electrodes to investigate the electrochemical performance of composite films with increased mass loading.

To make full use of symmetric supercapacitors for further in-series or in-parallel connection, it is necessary to reduce the resistance of the symmetric supercapacitors to the least. As shown in Figure S8a, specific areal capacitances of symmetric supercapacitors increase from 117.6 to 401.4 mF cm^{-2} with the increasing mass loading from 0.6 to 8.0 mg cm^{-2} at a large scanning rate of 50 mV s^{-1} . Although the composite films with higher mass loading exhibits higher specific areal capacitance (Figure S8a), the distance of ion-conduction pathway increased at the same time with the increase in the film thickness. The corresponding Nyquist plots of symmetric supercapacitors based on these composite films with increasing thickness (Figure S8b) show that the lowest equivalent resistance of 4.1Ω appeared at the mass loading of 1.6 mg cm^{-2} . Thus, further electrochemical tests were carried out on 1.6 mg cm^{-2} MNW70, MNF70, and CNT films.

2.3 Optimization of nanocellulose films for the editable supercapacitor

1 When the thickness of the electrode is too thick, the function of nanocellulose film as
2 the separator is not strong enough to avoid short circuit during editing process. Only after the
3 thickness of nanocellulose fiber film is larger than 5 μm , the as-prepared supercapacitor can
4 remain operative after editing process. However, increasing the thickness of nanocellulose
5 films on the electrode will lead to the larger distance between two electrodes, which increases
6 the infiltration resistance and the charge transfer resistance of the electrode-electrolyte
7 interfaces. As shown the Figure S13, a supercapacitor with thicker nanocellulose film results
8 in higher impedance that will decay the electrochemical performance of the editable
9 supercapacitors.

10

3. Supporting Figures

Figure S1 Schematics of preparation steps for MnO₂ nanoflowers and nanowires under normal and stirring hydrothermal method at 150 °C for 24 h respectively. (a) NH₄Cl and KMnO₄ dissolved in DI water in Teflon-lined autoclave. (b-c) Route 1 for the synthesis of the MnO₂ nanoflowers under static hydrothermal process. (d-e) Route 2 for the formation of ultralong MnO₂ nanowires through stirring hydrothermal process.

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References:

- [1] Y. Meng, Y. Zhao, C. Hu, H. Cheng, Y. Hu, Z. Zhang, G. Shi, L. Qu, *Adv. Mater.* **2013**, 25, 2326.
- [2] S. Y. Hong, J. Yoon, S. W. Jin, Y. Lim, S.-J. Lee, G. Zi, J. S. Ha, *ACS Nano* **2014**, 8, 8844.
- [3] M. Yu, Y. Zhang, Y. Zeng, M. S. Balogun, K. Mai, Z. Zhang, X. Lu, Y. Tong, *Adv. Mater.* **2014**, 26, 4724.
- [4] T. Lv, Y. Yao, N. Li, T. Chen, *Angew. Chem. Int. Edit.* **2016**, 55, 9191.
- [5] S. Wang, S. Yang, Z. Rong Dai, Z. L. Wang, *Phys. Chem. Chem. Phys.* **2001**, 3, 3750.
- [6] Y. Tang, Y. Zhang, J. Deng, J. Wei, H. Le Tam, B. K. Chandran, Z. Dong, Z. Chen, X. Chen, *Adv. Mater.* **2014**, 26, 6111.