

Mn₃O₄/Reduced graphene oxide based supercapacitor with ultra-long cyclic performance

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Materials and methods

Chemicals

MnCl₂·4H₂O (99.99%), sodium dodecyl sulfate (SDS) (≥ 98.5 %), sodium hydroxide (NaOH), were purchased from Sigma-Aldrich. Graphene oxide (GO, 5 mg mL⁻¹) was purchased from graphene supermarket. Carbon Nano Tube (CNT, 10 mg mL⁻¹) water dispersion was purchased from NanoAmor company. Distilled water and absolute ethanol were used in the experiments. The materials were used without further treatment.

Synthesis of Mn₃O₄ nanoparticles

In a typical synthesis procedure, sodium dodecyl sulfate (0.5 mmol) is firstly dissolved into 40 mL distilled water, and then MnCl₂·4H₂O (1 mmol) was dissolved into the above solution. Later, 10 mL of NaOH (0.5 mol L⁻¹) was added dropwise into the above solution. Next, the resulting suspension was stirred for 24 h and then aged for another 1 h. The precipitates obtained was gathered, washed with water and ethanol for three times and dried at 80 °C for 12 h to obtain final samples without further treatment. Before electrochemical test, the Mn₃O₄ nanoparticles were treated in a tube furnace (350 °C for 2 h under Ar and H₂) to enhance the crystallinity.

Synthesis of Mn₃O₄/RGO film paper

Briefly, certain Mn₃O₄ nanoparticles (20 mg) were mixed with 12 mL of distilled water and sonicated for 20 min to get a stable solution. Then 8 mL GO aqueous (5 mg mL⁻¹) was added into the above solution and sonicated for 20 min. The obtained suspension were transferred into a container with a mixed cellulose ester filter membrane in the bottle, and then the container was dried in vacuum under 60 °C to evaporate water, then peeled off to get a free-standing film paper. The dried film paper was annealed at 350 °C for 2 h under Ar and H₂ to reduce graphene oxide. The obtained products were labelled as MGP. As a reference, the pure reduced graphene oxide paper was fabricated under the same conditions except the addition of Mn₃O₄ nanoparticles, which was denoted as RGP.

Synthesis of CNT/RGO film paper

3 mL CNT (10 mg mL^{-1}), 6 mL GO aqueous (5 mg mL^{-1}) and 11 mL distilled water were mixed together and then sonicated for 20 min. Similarly, the obtained suspension was transferred into a container with a mixed cellulose ester filter membrane in the bottle, and then the container was put into an oven to evaporate water ($60 \text{ }^\circ\text{C}$). The dried film paper was then reduced at potential of -1.5 V for 10 h to reduce graphene oxide. The obtained product was denoted as CNP.

Characterization

Scanning electron microscopy (SEM) images were recorded on a ZEISS SEM Supra 40 (5 kV). SEM samples were prepared by dripping the sample solutions onto a silicon substrate. Transmission electron microscopy (TEM) was done on a JEOL-3010 (300 kV acceleration voltage). TEM samples were prepared by dripping the sample solutions onto a copper grid. The powder X-ray diffraction (XRD) pattern was measured by a powder diffractometer (Bruker D8 Advanced Diffractometer System) with a $\text{Cu K}\alpha$ (1.5418 \AA) source. Raman spectrometry were conducted for MGP and CNP on a Horiba MicroRaman HR Evolution System using an argon laser beam with an excitation wavelength of 514.5 nm . Surface composition was analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Analytical Axis UltraDLD UHV spectrometer with a monochromatized $\text{Al K}\alpha$ X-ray source (1486.6 eV) scanning a spot size of $700 \text{ }\mu\text{m}$ by $300 \text{ }\mu\text{m}$. Mass content was measured by thermal gravimetric analysis (SDT Q600).

Electrochemical measurements

All electrochemical tests were performed at room temperature. Cyclic voltammetry and galvanostatic charge/discharge measurement were conducted using an electrochemical system (Bio-logic VMP 3). To test the electrode material of pure Mn_3O_4 , Mn_3O_4 was mixed with polyvinylidene fluoride (PVDF), carbon black in a ratio of 8:1:1 with N-methyl-2-pyrrolidone (NMP). The mixture was hand-grinded for at least 10 min to obtain a slurry. The slurry was later coated onto carbon paper which served as a current collector. After heating at $80 \text{ }^\circ\text{C}$ overnight, the carbon paper was cut to $1 \text{ cm} \times 1 \text{ cm}$. The as-prepared film papers were utilized directly as a free standing electrode without any binder, conductive additive, or electric conductor. In the three-electrode system, saturated calomel electrode was used as the reference

electrode, platinum plate was served as the counter electrode, and 1M Na₂SO₄ was as the electrolyte. To test the electrode material of CNT/RGO film, CNT/RGO film was directly cut to 1 cm × 1 cm. The asymmetric supercapacitors were first characterized in a standard Swagelok 2-electrode cell configuration in 1M Na₂SO₄ aqueous electrolyte. One piece of MGP (1 cm in diameter) positive electrode and one piece of CNP (1 cm in diameter) negative electrode were immersed into the 1 M Na₂SO₄ aqueous. These two film electrodes were subsequently assembled together with a separator (normal filter paper) sandwiched in between. In order to evaluate the practical supercapacitor performance, the flexible asymmetric liquid-state supercapacitor was fabricated. The length and width of the films are 4 cm × 1 cm. For both CV and Charge/Discharge of full cell test, the measurement voltage was controlled in the range of 0 – 1.8 V for aqueous electrolyte test. Scan rates of 10, 25, 50, 100 and 200 mV s⁻¹ were used for CV, while the current densities of 0.1, 0.2, 0.5, 1, 2, 5, 10 and 20 A cm⁻³ were used for Charge/Discharge measurement.

The total gravimetric or volumetric capacitance of a supercapacitor in Farads per gram or per cubic centimeter were calculated from the galvanostatic discharge process according to the following equation:

$$F = I \Delta t / \Delta V \quad (1)$$

Where I is the current density (A g⁻¹ or A cm⁻³), Δt is the discharge time (s), and ΔV is the potential difference (V).

Based on the total volume of the active materials from the positive and negative electrode, energy density (E) and power density (P) were calculated based on the following formula.

$$E = \int_{t_1}^{t_2} V \cdot I \cdot t \, dt / 3.6 \quad (2)$$

$$P = 3600 E / \Delta t \quad (3)$$

Where V is the cell potential (V), I is the current density (A cm⁻³), t is the time (s), t₁ is the time which the cell is fully discharged, t₂ is the time which the cell is fully charged, Δt is the discharge time (s).

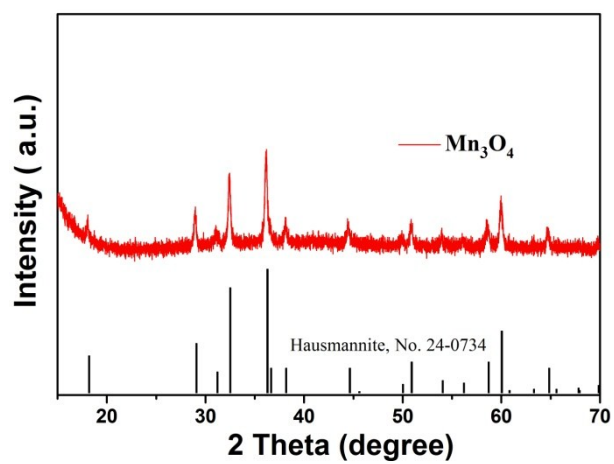


Fig. S1 XRD patterns of the obtained pure Mn_3O_4 .

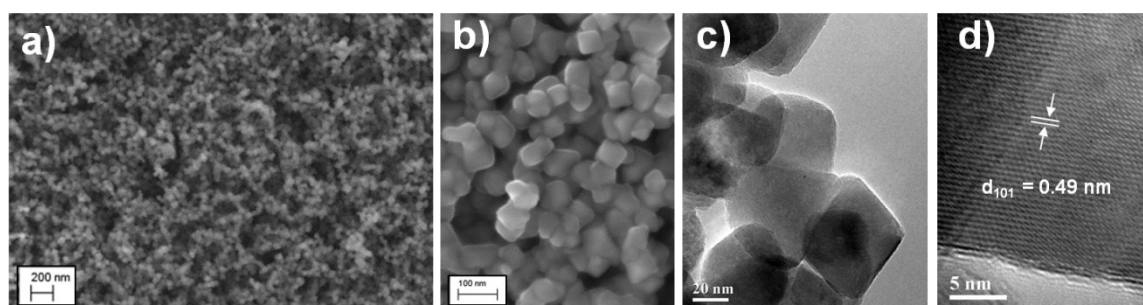


Fig. S2 a) and b) SEM images and c) and d) TEM images of the Mn_3O_4 nanoparticles.

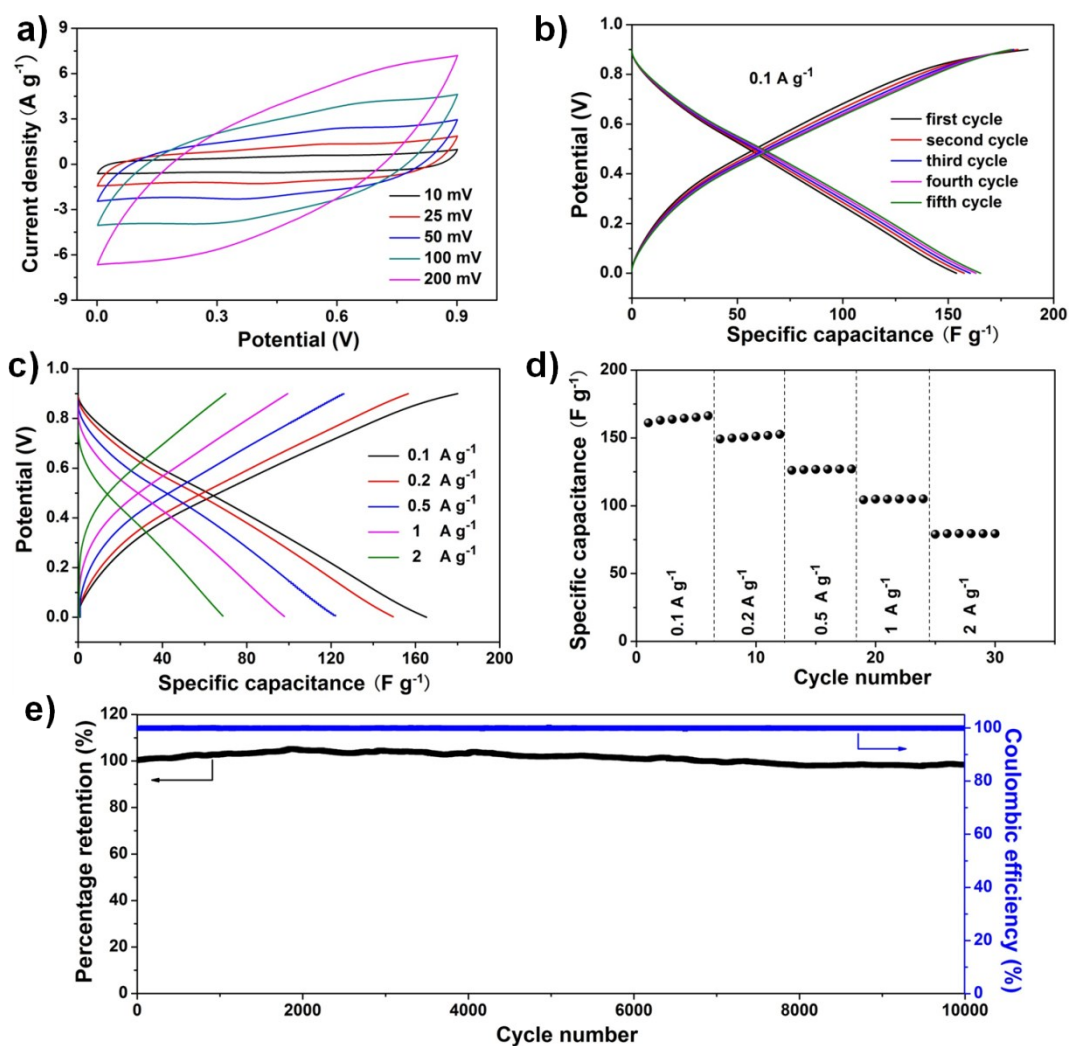


Fig. S3 Electrochemical performance of Mn₃O₄ nanoparticles in a three-electrode configuration with 1 M Na₂SO₄ as the aqueous electrolyte. a) CV curve at various scan rates; b) galvanostatic charge/discharge profiles at 0.1 A g⁻¹; c) galvanostatic charge/discharge profiles at different current densities 0.1 – 2 A g⁻¹; d) the rate performance at different current densities; e) the cyclic stability and coulombic efficiency at 1 A g⁻¹.

Table S1. Summary of supercapacitor performance parameters for Mn_3O_4 nanoparticles prepared by other methods.

Preparation method	Electrolyte	Potential window	Capacitance retention	references
hydrothermal method	1 M Na_2SO_4	-0.2–0.8 V	72.7% after 1000 cycles	1
hydrothermal method	1 M Na_2SO_4	0 – 1 V	70% after 1000 cycles	2
hydrothermal method	1 M Na_2SO_4	0 – 1V	78% after 5000 cycles	3
hydrothermal method	1 M Na_2SO_4	-0.4 – 0.6 V	88% after 1000 cycles	4
chemical precipitation method	1 M Na_2SO_4	-0.1 – 0.9 V	77% after 1000 cycles	5
a polyol method	1 M Na_2SO_4	-0.2 – 0.8 V	71.4% after 1500 cycles	6
air oxidation method	1M Na_2SO_4	0 – 0.9 V	100% after 10000 cycles	this work

These electrochemical tests were all performed in three electrode configurations.

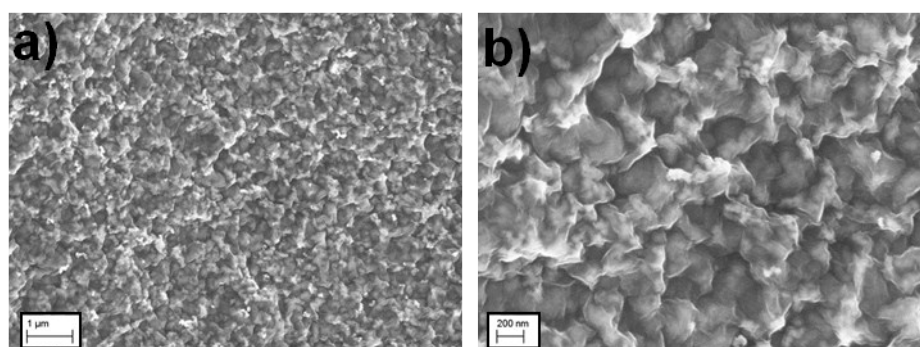


Fig. S4 SEM images of the surface structure of MGP.

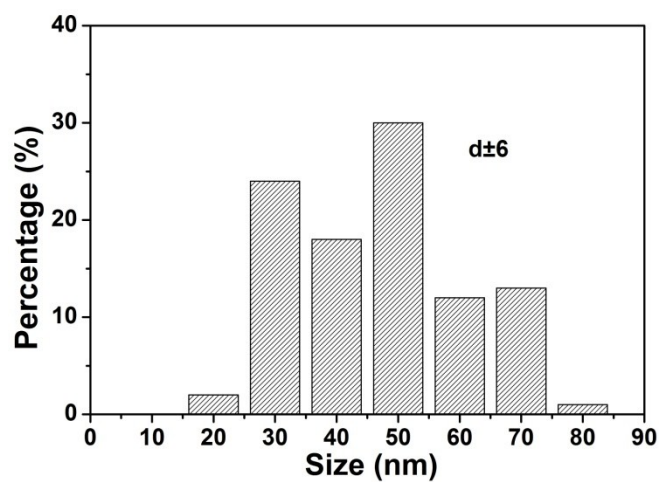


Fig. S5 The size distribution of Mn₃O₄ nanoparticles in MGP.

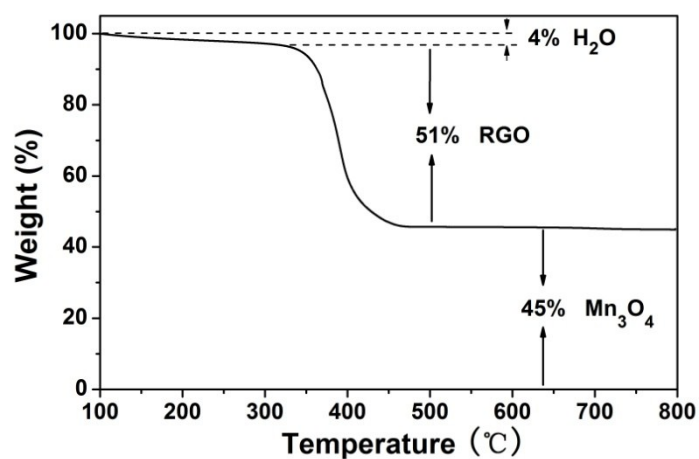


Fig. S6 DSC-TGA gravimetric analysis of MGP film paper to determine the weight percentage of Mn₃O₄ and RGO.

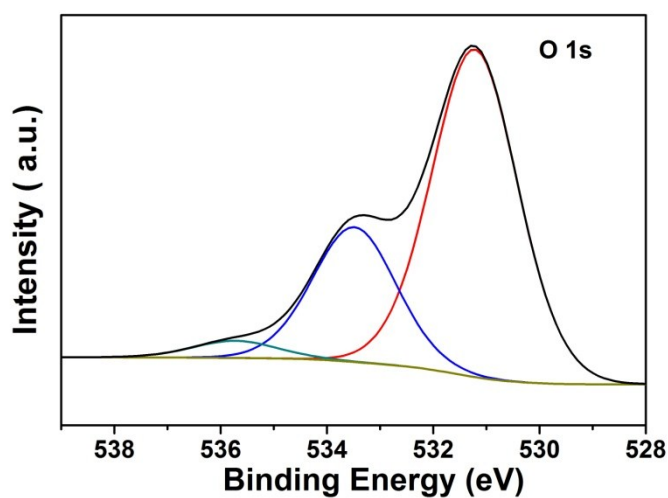


Fig. S7 XPS spectrum (O 1s) of MGP.

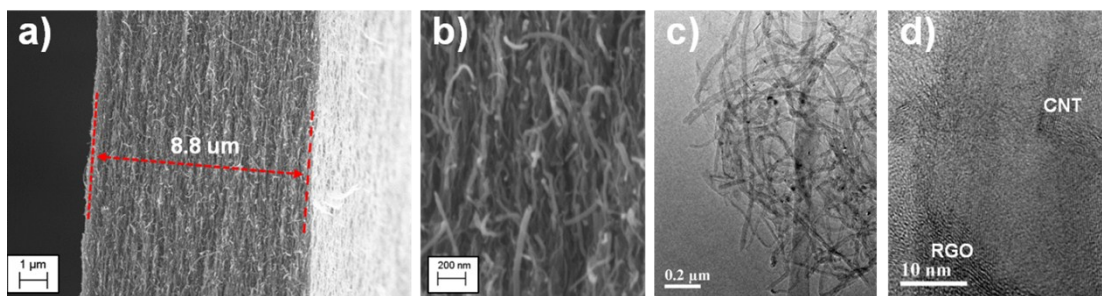


Fig. S8 a), b) SEM images and c), d) TEM images of the prepared CNP.

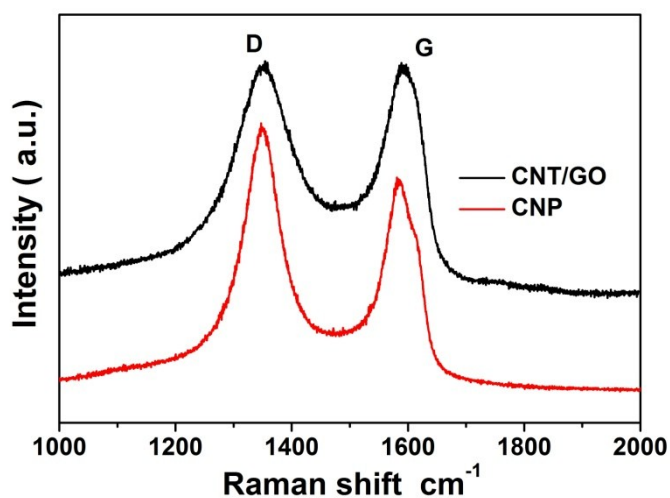


Fig. S9 Raman spectra for CNT/GO and CNP.

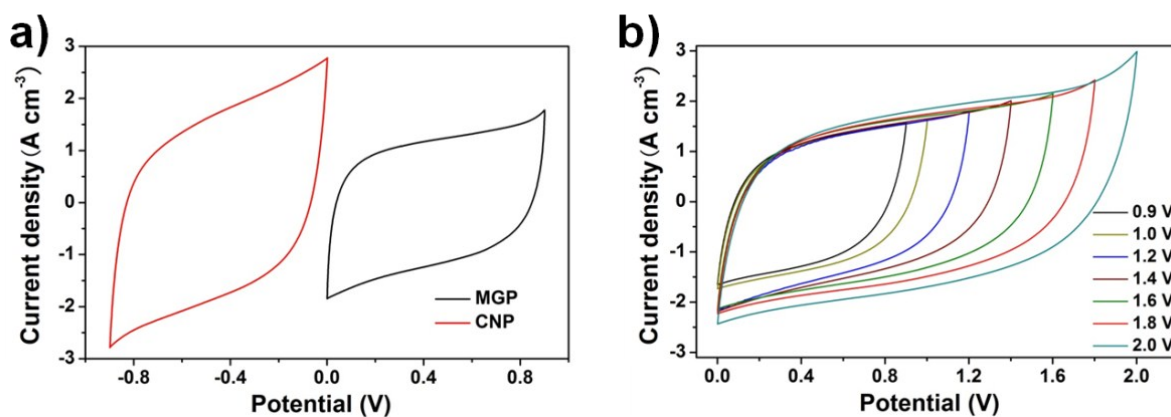


Fig. S10 a) CV curves of MGP and CNP tested separately in 1M Na_2SO_4 aqueous electrolyte conducted at 25 mV s^{-1} , b) CV curves of the MGP/CNP asymmetric supercapacitor in the range of 0.9-2.0 V.

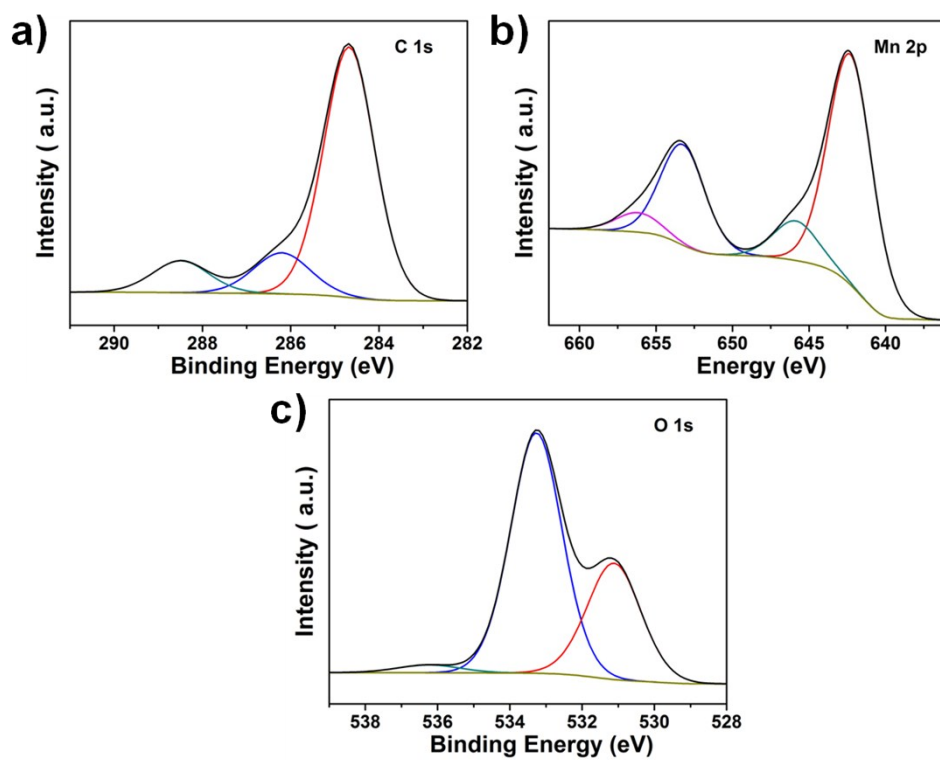


Fig. S11 XPS spectra of MGP after cyclic test. a) C 1s, b) Mn 2p and c) O 1s region.

Table S2. Summary of the supercapacitor performance parameters for Mn₃O₄-based materials.

Samples	Electrolytes	Potential window	Capacitance	Max Energy density	Max Power density	Capacitance retention	References
Mn ₃ O ₄ /graphene paper	Potassium polyacrylate /KCl	0–1.8 V	72.6 F g ⁻¹	32.7 Wh kg ⁻¹	9.0 kW kg ⁻¹	86.0% after 10000 cycles	7
Mn ₃ O ₄ /carbon nanofibers	1 M Na ₂ SO ₄	0–1.8V	Not reported	18 Wh kg ⁻¹	12 kW kg ⁻¹	94 % after 5000 cycles	8
Mn ₃ O ₄ /Carbon nanotubes	0.5 M Na ₂ SO ₄	0–2 V	25 F g ⁻¹	26.6 Wh kg ⁻¹	5.6 kW kg ⁻¹	103.9% after 1000 cycles	9
Mn ₃ O ₄ @nitrogen-doped graphene	EMIMBF ₄	0–4 V	56 F g ⁻¹	124.4 Wh kg ⁻¹	29.9 kW kg ⁻¹	82.4% after 10000 cycles (3.5V)	10
graphene/Mn ₃ O ₄ composites	Saturated K ₂ SO ₄	0–1 V	63 F g ⁻¹	8.7 Wh kg ⁻¹	1.0 kW kg ⁻¹	94 % after 1000 cycles	11
Mn ₃ O ₄ grown Ni/graphite/paper	Poly(vinyl alcohol)/NaOH gel	0–1.3 V	3.05 F cm ⁻³	0.35 mWh cm ⁻³	0.0325 W cm ⁻³	83.3 % after 12000 cycles	12
Mn ₃ O ₄ /rGO film	1 M Na ₂ SO ₄	0–2 V	54.6 F cm ⁻³	5.5 mWh cm ⁻³	6.86 W cm ⁻³	95% after 6000 cycles	13
Mn ₃ O ₄ /rGO film paper	1 M Na ₂ SO ₄	0–1.8 V	52.2 F cm ⁻³	18 mWh cm ⁻³	3.13 W cm ⁻³	115% after 60000 cycles	this work

These electrochemical tests were all performed in full cell configurations.

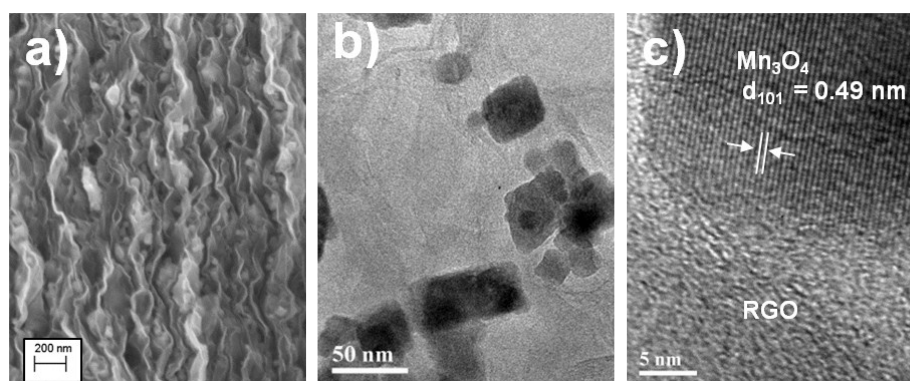


Fig. S12 a) SEM and b), c) TEM images of the MGP after cyclic test.

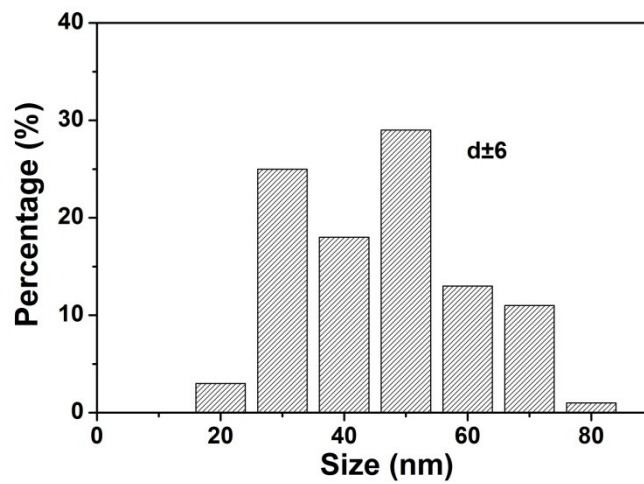


Fig. S13 The size distribution of Mn_3O_4 nanoparticles in MGP after cyclic test.

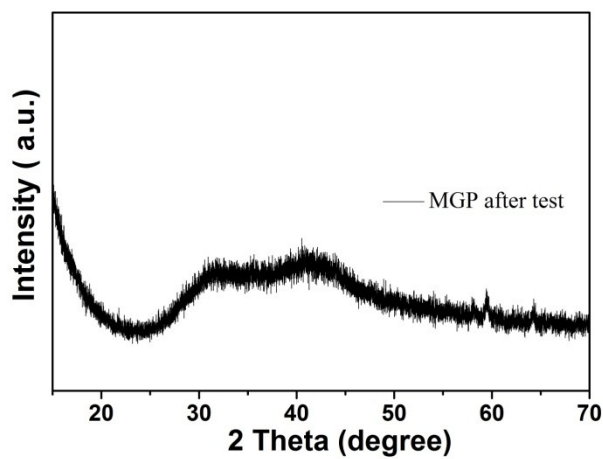


Fig. S14 XRD patterns of the MGP after cyclic test.

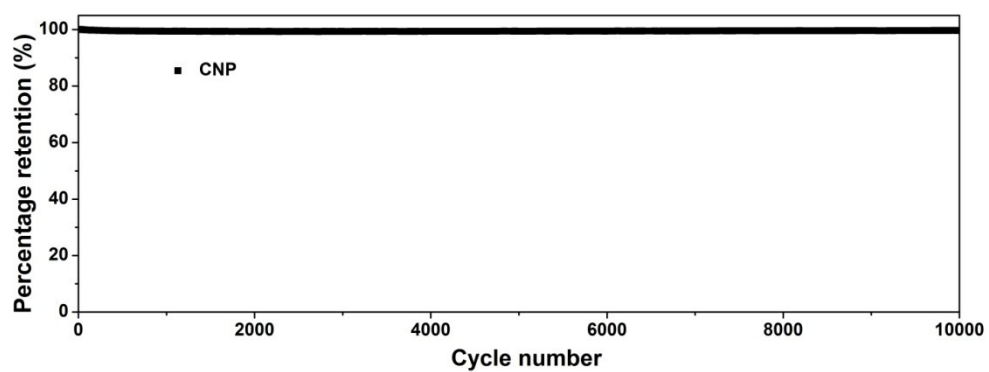


Fig. S15 The cyclic stability of CNP tested in a three-electrode configuration with 1 M Na_2SO_4 as the aqueous electrolyte at 5 A cm^{-3} .

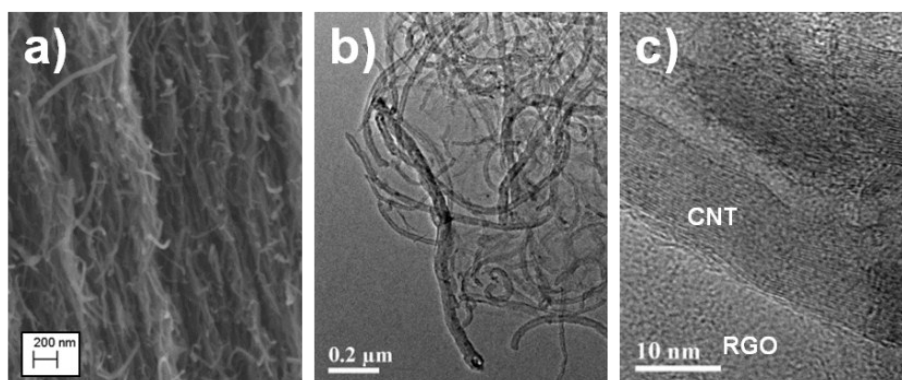


Fig. S16 a) SEM and b), c) TEM images of the CNP after cyclic test.

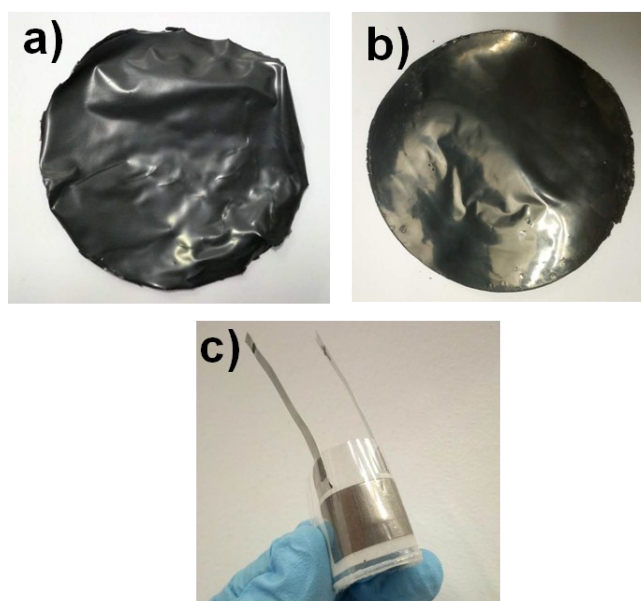


Fig. S17 a) a picture of MGP; b) a picture of CNP; c) optical photographs of the fabricated flexible liquid-state supercapacitor device with electrode area of $4\text{ cm} \times 1\text{ cm}$.

References

- 1 Y. Wu, S. Liu, H. Wang, X. Wang, X. Zhang and G. Jin, *Electrochim. Acta*, 2013, **90**, 210–218.
- 2 R. Dong, Q. Ye, L. Kuang, X. Lu, Y. Zhang, X. Zhang, G. Tan, Y. Wen and F. Wang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9508–9516.
- 3 F. Yang, M. Zhao, Q. Sun and Y. Qiao, *RSC Adv.*, 2015, **5**, 9843–9847.
- 4 C. Mondal, D. Ghosh, T. Aditya, A. K. Sasmal and T. Pal, *New J. Chem.*, 2015, **39**, 8373–8380.
- 5 B. G. S. Raj, A. M. Asiri, J. J. Wu and S. Anandan, *J. Alloys Compd.*, 2015, **636**, 234–240.
- 6 G. Jin, X. Xiao, S. Li, K. Zhao, Y. Wu, D. Sun and F. Wang, *Electrochim. Acta*, 2015, **178**, 689–698.
- 7 H. Gao, F. Xiao, C. B. Ching and H. Duan, *ACS Appl. Mater. Interfaces*, 2012, **4**, 7020–7026.
- 8 H. Wang, J. Deng, Y. Chen, F. Xu, Z. Wei and Y. Wang, *Nano Res.*, 2016, **9**, 2672–2680.
- 9 H. Cheng, H. M. Duong and D. Jewell, *RSC Adv.*, 2016, **6**, 36954–36960.
- 10 L. Liu, L. Su, J. Lang, B. Hu, S. Xu and X. Yan, *J. Mater. Chem. A*, 2017, **5**, 5523–5531.
- 11 F. Gao, J. Qu, Z. Zhao, Q. Zhou, B. Li and J. Qiu, *Carbon*, 2014, **80**, 640–650.
- 12 J. Feng, S. Ye, X. Lu, Y. Tong and G. Li, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11444–11451.
- 13 Y. Hu, C. Guan, G. Feng, Q. Ke, X. Huang and J. Wang, *Adv. Funct. Mater.*, 2015, **25**, 7291–7299.