

1D Hierarchical MnCo₂O₄ Nanowire@MnO₂ Sheet Core-shell Arrays on Graphite Paper as Superior Electrode for Asymmetric Supercapacitor

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1 **Abstract**

2 Heterostructured metal oxides core-shell architectures have attracted considerable
3 attention owing to their superior electrochemical performance in supercapacitors
4 compared to a single structure. Here, we report a simple and effective synthesis of
5 hierarchical MnCo₂O₄ nanowire@MnO₂ sheet core-shell nanostructures anchored on
6 graphite paper for use in supercapacitors. The proposed electrode exhibits a specific
7 capacitance of 2262 F g⁻¹ at 1 A g⁻¹. In addition, good rate capability and excellent
8 cycling performance are observed. An asymmetric supercapacitor with operating
9 potential at 1.6 V is demonstrated using MnCo₂O₄@MnO₂ as cathode and
10 graphene/nickel foam (NF) as anode. The MnCo₂O₄@MnO₂//graphene/NF
11 asymmetric device shows a high energy density of 85.7 Wh kg⁻¹ at a power density of
12 800 W kg⁻¹ while maintaining a high energy density of 34.7 Wh kg⁻¹ at 24 kW kg⁻¹.
13 Moreover, the device demonstrates a long-term cycling stability of 81.6% retention of
14 its initial specific capacitance.

15

16 **Introduction**

17

18 Many studies have focused on the development of high-performance electrochemical
19 energy storage devices to address the increasing energy demand and environmental
20 deterioration.^[1] Supercapacitors, a promising device for electrochemical energy
21 storage, have attracted significant research attention in recent years because of their
22 overall advantages over electrostatic capacitors and batteries in terms of their high
23 power density, long lifespan, rapid charge/discharge rates, safe operation, and
24 environmental friendliness.^[2] On the other hand, the relative energy density of
25 carbonaceous compound-based electrodes have hindered their applications in real

1 energy devices.^[3] Alternative pseudocapacitor materials, including conducting
2 polymers and transition metal oxides, have showed higher energy densities.^[4] In
3 particular, conducting polymers have a high energy density but low cycling stability.^[5]
4 In the search for high performance electrode materials available for supercapacitors,
5 binary metal oxides have shown great promise as an alternative for supercapacitor
6 electrodes because of the advantages of achievable mixed valences, and high
7 electrical conductivity relative to single component oxides,^[6] such as NiCo₂O₄,^[7]
8 MnCo₂O₄,^[8] CuCo₂O₄,^[9] ZnMn₂O₄,^[10] and CoMoO₄.^[11] MnCo₂O₄, in particular, has
9 attracted considerable interest in supercapacitor applications owing to its high
10 availability, low-cost and environmental friendliness.^[8] More significantly, MnCo₂O₄
11 has demonstrated excellent capacitive behaviour and high rate capability in
12 supercapacitors because cobalt has a higher oxidation potential, while manganese can
13 assume multiple oxidation states and bring in higher rate capacity.^[8] For example, Xu
14 et al. synthesized porous MnCo₂O₄ nanowires as a pseudocapacitor electrode in a 2 M
15 KOH aqueous solution, which exhibited a discharge capacitance of 1342 F g⁻¹ at 1 A
16 g⁻¹.^[12] Xia et al. produced Co_xMn_{3-x}O₄ nanorods and hollow octahedrons composites
17 from a simple hydrothermal method that displayed a capacitance of 266.8 F g⁻¹ at 5
18 mV s⁻¹ with good cycling performance (80.2 % remaining after 1000 cycles) for
19 supercapacitor applications.^[13] Wu et al. reported flower-like CoMn₂O₄ microsphere
20 architectures that showed a specific capacitance of 188 F g⁻¹ at 1 A g⁻¹ in a 1M
21 Na₂SO₄ solution with good cycling stability by retaining 93% of its original
22 capacitance after 1000 cycles.^[14]
23 Lightweight, low-cost, flexible supercapacitors with the capability of rapidly storing a
24 high energy density is an increasing trend towards portable electronics that is
25 effectively levelling the cyclic features of renewable energy sources. Currently,

1 commercial supercapacitors have suffered from drawbacks, such as (1) they can be
2 oxidized under ambient conditions, (2) have poor bend-ability, and (3) heavy weight
3 of the conductive substrates (nickel foam or copper foam), which have severely
4 limited the energy density of the overall electrode. In contrast, graphite paper is not
5 only highly conductive, but is also lightweight, low-cost, bendable, and inert under
6 ambient conditions. In addition, it can be woven to form wearable cloths,^[15] which is
7 attractive as an electrode material for flexible supercapacitors. In addition, active
8 electrochemical materials, such as NiCo₂O₄,^[7] NiCoAl-LDH/NiCo-carbonate
9 hydroxide^[15] and MnO_x/CNT/RGO,^[3a] have shown enhanced energy and power
10 densities after been grown directly on graphite paper, resulting in not only good
11 mechanical adhesion and electrical connection, but also avoiding the use of polymer
12 binders or conductive additives.

13

14 Recently, nanomaterials, particularly one-dimension core-shell heterostructures, have
15 proven to be an effective strategy for utilizing active materials in supercapacitors due
16 to the following advantages: Core-shell structure provides more active sites for
17 desirable electron transport pathways not only at the active materials surface but also
18 throughout the bulk. The open-network and free interspaces among these nanowire
19 arrays can be efficiently utilized, which shorten ion diffusion paths and improve the
20 utilization rate of electrode materials.^[16] In addition, the synergistic combination of
21 the virtues of the individual components for rich Faradaic redox reactions. For
22 example, Zou et al. reported mesoporous NiCo₂O₄@MnO₂ core-shell nanowire arrays
23 as an electrode showing a specific capacitance of 112 F g⁻¹ at 1 mA cm⁻².^[16] Huang
24 et al. reported core-shell ellipsoidal MnCo₂O₄ showing a large initial charge capacity
25 of 1433.3 mAhg⁻¹ at 0.1 A g⁻¹.^[17] Zhang et al. synthesized a hierarchical

1 ZnCo₂O₄@MnO₂ core–shell nanotube array electrode exhibiting a high areal
2 capacitances of 2.38 F cm⁻² at 6 mA cm⁻².^[18] On the other hand, there have been few
3 studies of the electrochemical capacitance of hierarchical heterostructured MnCo₂O₄
4 nanowires@MnO₂ nanosheets (MnCo₂O₄@MnO₂) core–shell architectures, even
5 though the individual capacitive properties of both have been investigated extensively.
6
7 In the present study, a new electrode design strategy was exploited to fabricate
8 integrated, binder-free and lightweight hierarchical MnCo₂O₄@MnO₂ core–shell
9 arrays anchored on functionalized graphite paper as cathode electrode in supercapacitor.
10 MnO₂ nanosheets were coated onto needle-like MnCo₂O₄ nanowire arrays as a
11 backbone on a flexible graphite paper support. The resulting hierarchical self-
12 supported MnCo₂O₄@MnO₂ core–shell arrays electrode delivered a high specific
13 capacitance of 2262 F g⁻¹ and 1103 F g⁻¹ at current densities of 1 A g⁻¹ and 20 A g⁻¹,
14 respectively, which are superior to those of the MnCo₂O₄ electrode at the same
15 current density. Moreover, the MnCo₂O₄@MnO₂ electrode also demonstrated good
16 cycling stability and showed an 87.1 % initial capacitance retention after 5000 cycles
17 at 10 A g⁻¹. An asymmetric supercapacitor (ASC) fabricated with MnCo₂O₄@MnO₂
18 and graphene/NF exhibited a cell voltage of 1.6 V with a specific capacitance of 241
19 F g⁻¹ at current density of 1 A g⁻¹, and maintained a high specific capacitance of 98 F
20 g⁻¹ at high current density of 30 A g⁻¹. Moreover, The ASC device delivered a high
21 energy density of 85.7 Wh kg⁻¹ at a power density of 800 W kg⁻¹. In addition, the
22 ASC device showed good stability towards long-term charge–discharge tests (81.6%
23 retention after 8000 cycles). The present MnCo₂O₄@MnO₂ heterostructure with
24 remarkable electrochemical properties makes it a potential electrode material for the
25 next generation high energy density supercapacitors.

1

2 **Experimental**

3 *Preparation of functionalized graphite paper*

4 All chemicals were used as purchased. The graphite paper was cleaned several times
5 with acetone, ethanol and deionized water, and dried at room temperature. According
6 to previous reports,^[19] graphite paper was functionalized via an electrochemical
7 corrosion method in a solution of 2 M H₂SO₄. A typical three-electrode configuration
8 measurement was conducted with graphite paper as the working electrode, platinum
9 sheet as the counter electrode and saturated calomel electrode (SCE: Hg/Hg₂Cl₂) as
10 the reference electrode. A constant voltage of 2.2 V was maintained for 20 min during
11 the corrosion process. Subsequently, the functionalized graphite paper was obtained

12

13 *Synthesis of hierarchical structure of MnCo₂O₄ nanowire arrays*

14 Hierarchical structure MnCo₂O₄@MnO₂ nanowires were synthesized by combining a
15 hydrothermal reaction and a thermal annealing process. In a typical synthesis
16 procedure, Mn(NO₃)₂·4H₂O (2 mmol), Co(NO₃)₂·6H₂O (4 mmol), urea (24 mmol),
17 and ammonium fluoride (10 mmol) were dissolved in deionized water (70 mL) with
18 vigorous magnetic stirring. After stirring for 1 h, the as-obtained solution was
19 transferred to a 100 mL Teflon container, and a piece of the functional graphite paper
20 substrate was then immersed into the reaction solution. The autoclave was sealed and
21 maintained at 120 °C for 5 h in an electric oven. After cooling naturally to room
22 temperature, the products on the graphite paper were carefully washed several times
23 with deionized water and absolute ethanol with ultrasonication, and then dried
24 overnight at 60 °C. Subsequently, the samples were calcined at 300 °C for 2 h at a

1 ramping rate of $2\text{ }^{\circ}\text{C min}^{-1}$ to transform the MnCo_2O_4 precursor to hierarchical
2 structured MnCo_2O_4 nanowires.

3

4 *Synthesis of hierarchical structure of $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ core–shell arrays*

5 The $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ core–shell structure was synthesised by a direct redox reaction
6 between the carbon and KMnO_4 . During thermal annealing, the MnCo_2O_4 precursor
7 was transformed to a MnCo_2O_4 nanowire, whereas carbon layer was coated on the
8 surface of the MnCo_2O_4 nanowire from the evaporation of graphite paper. Carbon
9 layer anchored to the surface of the MnCo_2O_4 nanowire works as a reducing agent to
10 reduce the KMnO_4 to MnO_2 nanosheets coated on the surface of the MnCo_2O_4
11 nanowire. In the process, the MnCo_2O_4 nanowire coated with carbon on graphite
12 paper was dispersed in 35 mL of a 0.02 M KMnO_4 solution and underwent a
13 hydrothermal process at 120°C for 2 h. After cooling naturally to room temperature,
14 the products on the graphite paper were washed carefully with deionized water and
15 absolute ethanol with ultrasonication and then dried at $50\text{ }^{\circ}\text{C}$ for 10 h. For comparison,
16 samples of MnCo_2O_4 nanowires grown on functionalized graphite paper were
17 obtained under the same conditions without adding KMnO_4 . In order to decrease the
18 uncertainty of the mass of the electrode, we prepared an active material on
19 functionlazed graphite paper with the size of $2 \times 4\text{ cm}^2$. Then, the total mass loadings
20 of MnCo_2O_4 and $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ on the graphite paper were 6.52 and 15.49 mg,
21 respectively.

22

23 *Materials characterization*

24 The chemical composition and crystallite phase of the as-synthesized products were
25 characterized by X–ray diffraction (XRD, D8–Discovery, Bruker) analysis using Cu

1 $K\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) at an accelerating voltage and current of 40 kV and 200 mA,
2 respectively. The XRD patterns were obtained over the range, $10\sim 80^\circ(2\theta)$, at a
3 scanning speed of $0.2^\circ/\text{s}$. The microstructure and morphology were examined by
4 scanning electron microscopy (SEM, Hitachi S-4800) and high resolution
5 transmission electron microscopy (HR-TEM, JEOL, JEM-2010F). The valence state
6 of the prepared samples was determined by X-ray photoelectron spectroscopy (XPS,
7 VG Scientifics ESCALAB250), which was calibrated to the carbon peak C 1s at
8 284.6 eV.

9

10 *Electrochemical measurement*

11 The electrochemical performance was measured on an IVIUM electrochemical
12 workstation system (Ivium, nState) using a three-electrode mode in a 6 M KOH
13 solution. The reference electrode and counter electrode were SCE and platinum,
14 respectively. Heterostructured $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ core-shell array electrode materials
15 or pristine MnCo_2O_4 electrode materials supported on the graphite paper were used
16 directly as the working electrode. The electrochemical tests of the ASC device were
17 performed on a two-electrode cell with $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode as positive
18 electrode and graphene/NF as negative electrode in a 6 M KOH aqueous electrolyte
19 solution. The CV curves were measured in the potential range between 0 and 0.5 V at
20 different scan rates from 2 to 50 mV s^{-1} . The galvanostatic charge/discharge processes
21 were performed by cycling the potential from 0 to 0.4 V at a range of current densities
22 (1, 2, 3, 4, 5, 8, 10, and 20 A g^{-1}). The cycling stability was evaluated by a
23 charge/discharge process at a current density of 10 A g^{-1} for more than 5000 cycles
24 over the voltage range, 0 to 0.4 V. The EIS data was collected over the frequency

1 range of 100 KHz to 0.01 Hz by applying an AC voltage with a 5 mV perturbation at
2 the open circuit potential.

3

4 **Results and discussion**

5

6 Fig. 1 presents the fabrication process for the hierarchical MnCo₂O₄@MnO₂ core–
7 shell arrays on graphite paper as supercapacitor electrode materials. First, graphite
8 paper was functionalized with oxygen functional groups, such as carbonyl, hydroxyl
9 and carboxylic (step 1). The MnCo₂O₄ precursor ((Co, Mn)OOH is shown in the Fig.
10 S1) nanowires were grown on functionalized graphite paper via a hydrothermal
11 process (step 2). During the thermal annealing process, the (Co, Mn)OOH nanowires
12 were transformed to MnCo₂O₄ nanowires, whereas carbon layer was coated on the
13 surface of the MnCo₂O₄ nanowires (step 3). Finally, MnCo₂O₄@MnO₂ arrays were
14 obtained by growing MnO₂ nanosheets onto the surface of the MnCo₂O₄ nanowires
15 via a second hydrothermal method. In a previous report, the growth of a MnO₂ shell
16 on active core materials was achieved by the impregnation of a glucose aqueous
17 solution and subsequent post-annealing in Ar gas to produce an amorphous carbon
18 layer on the active material surface, which acted as the carbon precursor for reduction
19 of KMnO₄ to MnO₂ by a chemical reaction between KMnO₄ and graphitic carbon
20 ($4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} = 4\text{MnO}_2 + \text{CO}_3^{2-} + 2\text{HCO}_3^-$).^[20] In the present study, the
21 growth of a MnO₂ shell on the active materials was achieved by utilizing the graphite
22 paper as the carbon source, in which a thin layer of carbon was coated on the surface
23 of the MnCo₂O₄ nanowires during the thermal annealing process of the graphite paper.
24 The porous MnO₂ nanosheets were then grown directly on the surface of the
25 MnCo₂O₄ nanowires arrays by dispersing MnCo₂O₄ nanowires arrays in 35 mL of a

1 0.02 M KMnO_4 solution and underwent a hydrothermal process at 120°C for 2 h,
2 forming high surface area heterostructured core-shell nanostructures, making them
3 fully available for the efficient Faradiac redox reaction. To verify the role of carbon
4 layer for reduction of KMnO_4 to MnO_2 on the surface of MnCo_2O_4 nanowires arrays,
5 MnCo_2O_4 nanowires arrays grown on Ni foam were put in 35 mL of a 0.02 M KMnO_4
6 solution and underwent the same hydrothermal process. Fig. S2 (Supplementary
7 Information) shows the SEM images of the (Co, Mn)OOH (Fig. S2a-b), MnCo_2O_4
8 nanowires arrays (Fig. S2c-d) and MnCo_2O_4 nanowires arrays after second
9 hydrothermal growth in KMnO_4 solution on Ni foam (Fig. S2e-f). Results showed
10 clearly that MnO_2 shell did not form on the surface of the MnCo_2O_4 nanowires arrays,
11 confirming the importance of the carbon layer for reduction of KMnO_4 to MnO_2 on
12 the surface of MnCo_2O_4 nanowires arrays.

13

14 The crystal phase of the $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ structure was analysed by XRD, as shown
15 in Fig. 2a. All the diffraction peaks of the MnCo_2O_4 nanowires were indexed to the
16 JCPDS card no. 1-1130. Moreover, the characteristic peaks located at 21.8° , 28.0° ,
17 35.1° , 36.8° , and 42.1° 2θ were assigned to the (101), (201), (301), (210), and (002)
18 planes of the MnO_2 (JCPDS card no. 39-375), respectively, confirming the existence
19 of the $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ heterostructure by this approach. The detailed
20 microstructures of the $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ arrays were examined by TEM.

21

22 Fig. 2b and c shows the XPS spectrum of the $\text{MnCo}_2\text{O}_4@ \text{MnO}_2$ core-shell structure,
23 which were calibrated with reference to the C 1s peak at 284.6 eV. The Mn 2p XPS
24 spectrum revealed three kinds of manganese species that were assigned to species
25 containing Mn^{2+} , Mn^{3+} and Mn^{4+} ions (Fig. 2b). In particular, the fitting peaks at

1 binding energies of 641.5 and 653.4 eV were ascribed to Mn^{2+} , whereas the peaks at
2 643.5 and 654.5 eV were assigned to Mn^{3+} .^[21] Moreover, the Mn 2p spectrum was
3 best fitted to two major peaks at binding energies of 654.4 and 642.6 eV with a spin-
4 energy separation of 11.8 eV, which was assigned to Mn^{4+} .^[22] Similarly, the Co 2p
5 emission spectrum (Fig. 2c) was best fitted with two spin-orbit doublets, which could
6 be observed at 780.5 and 795.8 eV, respectively, demonstrating the presence of both
7 Co^{2+} and Co^{3+} species.^[23] In addition, the synthetic effects of the MnO_2 shell and
8 MnCo_2O_4 core provide not only richer redox couples, $\text{Mn}^{4+}/\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$,
9 but also many electroactive sites in the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ structures, which is
10 beneficial to the long-term cycling stability and high rate capacity of the
11 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode.

12

13 SEM and TEM were used to examine the structure and morphology of the as-prepared
14 materials. As shown in a low-magnification SEM image in Fig. 3a and b, the (Co,
15 Mn)OOH nanowires with a needle-like shape were grown densely on the graphite
16 paper surfaces. A close observation of the nanowire showed that the individual (Co,
17 Mn)OOH nanowires have a mean diameter of approximately 50 nm and a length of up
18 to several microns (Fig. 3c). After calcination at 300 °C for 2 h in air (Fig. 3d-f),
19 wiregrass-like MnCo_2O_4 nanowires preserved the original morphology with a similar
20 length and dimensions. Fig. 3g shows that the as-prepared $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ arrays
21 were grown uniformly over surface of the graphite paper with a mean diameter of
22 approximately 135 nm and lengths of around several microns. High-magnification
23 SEM showed that highly dense MnO_2 nanosheets were grown uniformly over the
24 surfaces of the MnCo_2O_4 nanowires backbone and closely connected to each other to
25 form a continuous open-network structure (Fig. 3h and i). The existence of graphite

1 paper supporter was verified by the Fig. S3. Such a design has several advantages: (1)
2 the nanosheets allow for a short diffusion length of ions and maintain the structural
3 integrity of the core during the charge/discharge process; (2) the 1D nanowires serve
4 as both the backbone and electron superhighway for charge transport; and (3) the
5 interconnected open-network core-shell features leading to huge exposed surface
6 areas between the electrode and electrolyte lead to the efficient utilization of electrode
7 materials, thus contributing to a high specific capacitance;^[24]

8

9 Fig. 4 presents TEM images of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ structure. The surfaces of the
10 MnCo_2O_4 nanowires were covered uniformly by thin interconnected sheet-like
11 subunits with a thickness of approximately several nanometres, as confirmed by the
12 TEM images in Fig. 4a. Fig. 4b shows that MnCo_2O_4 nanowire possesses a porous
13 structure with wormhole-like nanopores, which were attributed to nanopores
14 generated as H_2O and gases were released from the decomposition of precursors by
15 thermal annealing. Significantly, the nanopores structure can allow the efficient
16 diffusion of electrolyte ions. Moreover, within such unique hierarchical core-shell
17 nanowires, the open and free interspaces among these MnCo_2O_4 nanowires arrays can
18 be utilized efficiently, which will allow easier access of the electrolyte ions to the
19 surface of the active materials and improve the utilization rate of the electrode
20 materials. Therefore, a high electrochemical performance resulting from a
21 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ structure is expected. Furthermore, the selected area electron
22 diffraction (SAED) pattern of the MnO_2 nanosheets confirmed the single-crystalline
23 nature (Fig. 4c), which corresponds to the planes of ramsdellite-type MnO_2 (JCPDS
24 39-375), as shown in the XRD data. The HRTEM image of the MnCo_2O_4 core (Fig.
25 4d) showed that the d-spacing of 0.204 nm corresponds to the distance of the (400)

1 plane of the MnCo_2O_4 nanowire crystal, whereas the MnO_2 nanosheet showed a
2 lattice spacing of 0.225 nm, which corresponds to the (311) interplanar spacing of
3 MnO_2 . Energy-dispersive X-ray spectroscopy (EDS) of the individual sample further
4 revealed O, Co and Mn distributed uniformly over the structure (Fig. 4e). The
5 corresponding EDS element maps showed that Co was located mostly in the inner
6 areas of the core-shell architecture, whereas Mn and O were distributed in the entire
7 regions, confirming the hierarchical core-shell structure of $\text{MnCo}_2\text{O}_4@\text{MnO}_2$.

8

9 To demonstrate the electrochemical superiority of the proposed heterostructured
10 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode, electrochemical studies of the electrode were conducted
11 in a three-electrode configuration using a 6 M KOH solution as the electrolyte with Pt
12 and Hg/HgO as the counter and reference electrodes, respectively. Fig. 5a shows the
13 comparison of CV curves of MnCo_2O_4 , $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ to the background signal
14 from the graphite paper over a potential window between 0 and 0.5 V at a scan rate of
15 10 mV s^{-1} . The typical curve exhibited obvious pseudocapacitance features with one
16 pair of well-defined redox peaks, suggesting that the capacitance characteristics are
17 controlled by a reversible Faradaic redox reaction, which is very different from that of
18 carbon with a rectangular CV curve. It should be noted that the graphite paper has
19 negligible contribution to the capacitance of the whole electrode (about 7.84 % for
20 MnCo_2O_4 samples and 5.29 % for $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ samples). The CV integrated
21 area of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode was apparently larger than that of the
22 MnCo_2O_4 , indicating that the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode has a significantly larger
23 specific capacitance than the unitary MnCo_2O_4 electrode. The CV curves of the
24 MnCo_2O_4 nanowires (Fig. 5b) revealed an anodic peak at approximately 0.24 V and
25 the cathodic peak at 0.14 V, which were assigned to oxidation on $\text{Co}^{2+}/\text{Co}^{3+}$ and

1 reduction on Mn^{3+}/Mn^{4+} through the possible electrochemical reactions reported
2 earlier.^[25] The CV curves of the $MnCo_2O_4@MnO_2$ electrode (Fig. 5c) revealed a pair
3 of redox reaction peaks at 0.35 V and 0.2 V, which resulted mainly from redox
4 reactions related to $M-O/M-O-ON$, where M represents Co or Mn ions and N
5 represents H or K ions.^[16, 26] A similar shift of the redox reaction peaks to lower and
6 higher potential ends was reported in $ZnCo_2O_4@MnO_2$ core-shell structure.^[18]
7 Compared to the CV curves of $MnCo_2O_4$, the area integrated within the CV curve of
8 $MnCo_2O_4@MnO_2$ electrode was higher than that of the $MnCo_2O_4$ electrode,
9 suggesting a much higher pseudocapacitance. It is noteworthy to point out that
10 variations in redox peak positions of these two samples, which can be ascribed to the
11 difference in the polarization behaviour and the Ohmic resistance of the electrodes
12 during the CV tests.^[27] Interestingly, the shape retention of the CV curves, even at a
13 high scan rate of 50 mV s^{-1} with only a slight shift in the redox peaks due to electrode
14 polarization, indicated that the $MnCo_2O_4@MnO_2$ electrode is in favour of fast redox
15 reactions and possesses better reversibility.^[28] An almost linear relationship for the
16 $MnCo_2O_4$ and $MnCo_2O_4@MnO_2$ electrodes was observed between the cathodic peak
17 current density and the square root of the applied scan rate, as shown in Fig. 5d,
18 indicating that the electrochemical reactions in the electrodes are controlled by the
19 diffusion process of OH^- ion and surface redox reactions taking place in the charge
20 storage process. Specifically, the apparent diffusion coefficient (D) of OH^- ion is
21 calculated in prepared materials employing Randles-Sevcik equation,^[29]

$$22 \quad I_p = 2.69 \times 10^5 \times n^{\frac{3}{2}} \times A \times \sqrt{D} \times Co \times \sqrt{v} \quad (1)$$

$$23 \quad D(MnCo_2O_4 @ MnO_2) / D(MnCo_2O_4) = [(I_p / \sqrt{v})(MnCo_2O_4 @ MnO_2) / (I_p / \sqrt{v})(MnCo_2O_4)]^2$$

$$24$$

$$25 \quad = (12.6946/11.5785)^2 = 1.202 \quad (2)$$

1 where I_p is the peak current, n is the number of electrons involved in the reaction, A is
2 the surface area of the electrode, D is the diffusion coefficient of the electrode
3 material, C_0 is the proton concentration and v is the scanning rate. The diffusion
4 coefficient of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ composite electrode ($D_{\text{MnCo}_2\text{O}_4@\text{MnO}_2}$) was 1.202
5 time larger than that of the MnCo_2O_4 electrode ($D_{\text{MnCo}_2\text{O}_4}$), confirming the faster
6 diffusion of OH^- and protons, and the decrease in electrode polarization in the host
7 materials for higher electrochemical behaviour.^[30]

8

9 Fig. 6a shows the galvanostatic discharge/charge (GCD) curves for the MnCo_2O_4 and
10 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrodes at the same current density of 1 A g^{-1} . As expected, the
11 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode showed a much longer discharging time than that of the
12 MnCo_2O_4 electrode. This means that the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode material exhibits
13 a higher specific capacitance than the MnCo_2O_4 electrode material. The GCD curves
14 (Fig. S4, Supplementary Information) of the MnCo_2O_4 electrode at different current
15 densities from 1 to 20 A g^{-1} show a deviation from the typical triangular shape of the
16 EDLCs indicating the Faradaic characteristics of charge storage. The shoulders in the
17 charge-discharge graphs at 0.3 V during charging and 0.2 V during discharging
18 indicate the redox reactions, which are consistent with the CV curves. For the
19 MnCo_2O_4 electrode, specific capacitances of 1575, 1442, 1299, 1228, 1171, 1036,
20 923, 776, and 685 F g^{-1} at current densities of 1, 2, 3, 4, 5, 8, 10, 15, and 20 A g^{-1}
21 were obtained. The $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode delivered a high pseudocapacitance of
22 2262, 1906, 1734, 1604, 1503, 1374, 1278, 1181, and 1103 A g^{-1} at current densities
23 of 1, 2, 3, 4, 5, 8, 10, 15, and 20 A g^{-1} , respectively. The GCD curves (Fig. 6b) of the
24 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode showed a similar shape to that of the MnCo_2O_4 electrode
25 but with a slightly elevated discharge/charge plateau, which is consistent with the CV

1 curves. Remarkably, the capacitance of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode outperforms
2 than that of the MnCo_2O_4 electrode at various discharge/charge rates (Fig. 6c). The
3 specific capacitance retention was 48.8 % for the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode
4 compared to 43.5 % for the MnCo_2O_4 electrode when the current density was
5 increased from 1 to 20 A g^{-1} , which indicates the efficient utilization of the
6 underlying MnCo_2O_4 nanowires despite being covered by the MnO_2 nanosheets.
7 Furthermore, the specific capacitance of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode was much
8 higher than those previously reported for directly-grown pseudocapacitive materials,
9 such as MnCo_2O_4 nanowires (1342 F g^{-1} at 1 A g^{-1}),^[12] MnCo_2O_4 nanowire@reduced
10 graphene oxide (334 F g^{-1} at 1 A g^{-1}),^[30a] Mn–Ni–Co ternary oxide nanowires (638 F
11 g^{-1} at 1 A g^{-1}),^[31] carbon-modified MnO_2 nanosheet (638 F g^{-1} at 0.25 mA cm^{-2}),^[32]
12 and MnO_2 nanosheet@graphene (267 F g^{-1} at 0.2 A g^{-1})^[1]. On the other hand, the
13 present $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ heterostructured nanowires showed higher capacitance than
14 other core–shell nanostructures, such as CuCo_2O_4 nanowire@ MnO_2 nanoflake (327 F
15 g^{-1} at 1.25 F g^{-1}),^[33] $\text{ZnO}@\text{Co}_3\text{O}_4$ core–shell nanowires (857.7 F g^{-1} at 1 A g^{-1})^[34],
16 hierarchical CuO nanotube@ MnO_2 nanosheet (276 F g^{-1} at 0.6 F g^{-1}),^[22] Ni_3S_2
17 nanorod@ $\text{Ni}(\text{OH})_2$ nanosheet (1037.5 F g^{-1} at 5.1 F g^{-1}),^[35] and $\text{NiCo}_2\text{O}_4@\text{NiS}$
18 nanoplate (926 F g^{-1} at 6.15 F g^{-1}),^[36] etc. Such high pseudocapacitor at large current
19 densities highlights the great advantages of the present core–shell architecture. The
20 superior electrochemical properties of the proposed $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode are
21 explained as follow: (1) core–shell structure provides more active sites for efficient
22 electrolyte ion transportation not only on the surface of active materials but also
23 throughout the bulk; (2) the open-network and free interspaces among these nanowire
24 arrays can be efficiently utilized, which facilitate the electrolyte ions access the
25 surface of active materials more easily and improve the utilization rate of electrode

1 materials;^[16] (3) the enhanced electrochemical performance could be attributed to the
2 synergistic effects of two different components;^[27b] (4) 1D nanowire core serves as an
3 efficient backbone for charge transport^[24], while 2D shell provides a high surface area
4 for short diffusion paths of ions and maintains the structural integrity of the core
5 during the charge/discharge process; (5) cobalt has a higher oxidation potential, while
6 manganese has multiple oxidation states leading to higher rate capacity.^[8]

7

8 The electrochemical stability of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode was examined by
9 cycling processes. As shown in Fig. 6d, the cycling stability was enhanced largely in
10 the core-shell heterostructure. The overall capacitance loss for MnCo_2O_4 was
11 approximately 19.9 % after 5000 cycles, whereas it was only 12.9 % after 5000 cycles
12 for the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode. Therefore, the proposed heterostructured
13 nanowire arrays electrode have potential excellent electrochemical stability for long
14 cycle life applications at high current densities. Such intriguing capacitive behaviour
15 was attributed to the unique 1D hierarchical core-shell nanowires arrays configuration
16 and the synergistic pseudocapacitive contributions from the MnCo_2O_4 nanowires core
17 and the ultrathin MnO_2 sheets shell. Fig. 6e presents the GCD curves of the as-
18 fabricated $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode for the last 6 cycles. Even after a long period
19 of the 5000 GCD tests, the results showed that the as-fabricated electrode maintained
20 good electrochemical reversibility with approximately 98.7 % Coulombic efficiency
21 and remained undistorted and essentially symmetrical. Fig. 6f shows the CV curves of
22 the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode before and after 5000 cycles at 5 mV s^{-1} . A slight
23 decrease in the integrated area of the CV curves of the two electrodes indicates the
24 long-term stability of $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrode.

25

1 To further evaluate the electrochemical behaviour, EIS was carried out to reveal the
2 kinetics of the MnCo₂O₄@MnO₂ electrode. EIS was performed over the frequency
3 range, 100 kHz to 0.01 Hz. Fig. S5 presents the Nyquist plots of the MnCo₂O₄ and
4 MnCo₂O₄@MnO₂ electrodes at the open circuit potential. All the Nyquist plots show
5 typical electrochemical capacitor behaviour with a semicircle in the high frequency
6 region, which indicates charge transfer resistance between the electrolyte and the
7 electrode interface. The inset of Fig. 5 clearly showed that the MnCo₂O₄@MnO₂
8 electrode has a lower equivalent series resistance (R_s) of 0.30 Ω compared to that of
9 the MnCo₂O₄ electrode (0.48 Ω). Moreover, the MnCo₂O₄@MnO₂ electrode also
10 showed a smaller charge transfer resistance, R_{ct} , of 3.71 Ω , than that of the MnCo₂O₄
11 electrode (5.52 Ω), which suggests a lower internal resistance and charge transfer
12 resistance of the MnCo₂O₄@MnO₂ electrode. That is important for high
13 electrochemical activity for energy storage.^[37]

14

15 To evaluate the feasibility of such MnCo₂O₄@MnO₂ core-shell electrode, an ASC
16 device is assembled by using MnCo₂O₄@MnO₂ as a positive electrode materials and
17 graphene coating on the porous nickel foam (graphene/NF) as the negative electrode.
18 Significantly, the optimal mass ratio of positive and negative electrodes was fixed to
19 0.32, which is based on the charge balance between the two electrodes (Fig. S6,
20 Supporting Information). A series of CV measurements of
21 MnCo₂O₄@MnO₂//graphene/NF ASC device in different voltage windows at 50 mV
22 s⁻¹ were carried out to estimate the best operating potential (Fig. 7a). With an increase
23 of the operating potential to 1.6 V, a slight hump can be observed, indicating some
24 irreversible reactions happen when potential window higher than 1.6V.^[38] CV curves
25 of the ASC device at different scan rates ranging from 5 to 50 mV s⁻¹ were given in

1 Fig. 7b. The consistent CV curves of ASC device at various scan rates exhibit a
2 combination of both pseudocapacitive and electric double-layer types of capacitance.
3 Galvanostatic charge/discharge curves showed nonlinear lines, indicating the
4 pseudocapacitance behaviour of the electrode materials (Fig. 7c). The specific
5 capacitance was calculated to be approximately 241, 204, 197, 185, 174, 156,
6 145, 126, 114, and 98 F g^{-1} at current densities of 1, 2, 3, 4, 5, 8, 10, 15, 20, and 30 A
7 g^{-1} , respectively (based on the total mass of the active material in the positive and
8 negative electrodes), showing a good rate capability (Fig. 7d). The Nyquist plot of the
9 $\text{MnCo}_2\text{O}_4@\text{MnO}_2//\text{graphene/NF}$ ASC device was shown in Fig. S7. The equivalent
10 series resistance of the ASC device is around 1.02Ω , with a slight charge transfer
11 resistance of 0.74Ω . The results indicate an good ion transport properties of the
12 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ core-shell electrode.

13
14 Schematic diagram of the ASC device was illustrated using the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ on
15 the graphite paper electrode as the cathode and the graphene on Ni foam as the anode
16 in a 6 M KOH, and a piece of cellulose paper was used as the separator (Fig. 8a).
17 Long term cycling stability is also a critical parameter for practical application of
18 supercapacitors. The cycling was performed using charge/discharge test at current
19 density of 10 A g^{-1} up to 8000 cycles (Fig. 8b). The $\text{MnCo}_2\text{O}_4@\text{MnO}_2//\text{graphene/NF}$
20 ASC device shows an outstanding cycling stability and demonstrates 81.6% of the
21 specific capacitance retention (comparing with the second cycle). Moreover, The
22 charge/discharge curves of the initial 10 cycles were shown in the inset of Fig. 8b,
23 from which the discharge curve is almost identical with its corresponding charge
24 counterpart (Fig. S8), implying that an excellent electrochemical reversibility and
25 Coulombic efficiency of the device. To further illustrate the energy and power

1 properties of the present devices, Ragone plot was plotted derived from
2 charge/discharge data as shown in the Fig. 8c. The $\text{MnCo}_2\text{O}_4@\text{MnO}_2//\text{graphene}/\text{NF}$
3 ASC device showed a maximum energy density of 85.7 Wh kg^{-1} at a power density of
4 800 W kg^{-1} , while it maintained a high energy density of 34.7 Wh kg^{-1} at a power
5 density of 24 kW kg^{-1} . The results showed a much enhanced energy density at high
6 power density as compared with previously reported ASC devices such as a-
7 $\text{Co}(\text{OH})_2@\text{Co}_3\text{O}_4//\text{AC}$ (13.5 Wh kg^{-1} at 145 W kg^{-1}),^[39] $\text{CoMoO}_4@3\text{Dgraphene}/\text{AC}$
8 (21.1 Wh kg^{-1} at 300 W kg^{-1}),^[40] $\text{NiCo}_2\text{O}_4@\text{MnO}_2//\text{AC}$ (35 Wh kg^{-1} at 163 W kg^{-1}),^[16]
9 $\text{NiCo}_2\text{O}_4\text{-rGO}/\text{AC}$ (23.3 Wh kg^{-1} at 324.9 W kg^{-1}),^[41] (MnNiCo) oxide//C (29 Wh
10 kg^{-1} at 188 W kg^{-1}),^[31] $\text{Ni}_x\text{Co}_{3-x}$ oxide//AC (37.4 Wh kg^{-1} at 163 W kg^{-1}),^[38]
11 $\text{Ni}(\text{OH})_2@\text{MnO}_2@\text{rGO}/\text{rGO}$ (54 Wh kg^{-1} at 392 W kg^{-1}),^[42]
12 $\text{graphene}@\text{MnO}_2/\text{graphene}$ (25.2 Wh kg^{-1} at 100 W kg^{-1}).^[43] Obviously, the
13 exceptional energy density property of $\text{MnCo}_2\text{O}_4@\text{MnO}_2//\text{graphene}/\text{NF}$ ASC device
14 might be related to the advantageous merit of core-shell structure. It is noted that the
15 interconnected MnO_2 nanosheets building blocks grown on MnCo_2O_4 nanowire arrays
16 give rise to a highly porous morphology, which provides more active sites for
17 efficient electrolyte ion access not only at the active materials surface but also
18 throughout the bulk. To further demonstrate the potential application of the present
19 ASC device, two devices were connected in series to power a red light-emitting diode
20 (Fig. 8d).

21

22

23 **Conclusions**

24

1 In summary, 1D hierarchical MnCo₂O₄ nanowire@MnO₂ nanosheet core-shell
2 nanowire arrays were fabricated using a facile and cost-effective strategy for
3 supercapacitor applications. The results showed that this heterostructured electrode
4 displays a high specific capacitance of 2262 F g⁻¹ at a discharge current density of 1
5 A g⁻¹ (~ 0.4 fold increase in specific capacitance with respect to the pristine
6 MnCo₂O₄ nanowire arrays). In addition, this 1D hierarchical heterostructured
7 electrode exhibited good long-term cycling stability at a high charge-discharge
8 current density of 10 A g⁻¹ (~ 87.1 % of its initial specific capacitance was retained
9 after 5000 cycles), which were better than those of the pure MnCo₂O₄ nanowire arrays.
10 The improved performance indicates a desired structure derived from a synergistic
11 contribution from the MnCo₂O₄ nanowire core and MnO₂ nanosheet shell. An ASC
12 device based on MnCo₂O₄@MnO₂//graphene/NF configuration was demonstrated to
13 deliver high specific energy densities at various power densities. The asymmetric
14 supercapacitor showed a high energy density of 85.7 Wh kg⁻¹ at a power density of
15 800 W kg⁻¹ and 34.7 Wh kg⁻¹ at a high power density of 24 kW kg⁻¹. Moreover, the
16 ASC device exhibited an outstanding cycling life of 81.6% of its initial specific
17 capacitance after 8000 cycling.

18

19

1 **Acknowledgements**

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3 National Research Foundation of Korea (NRF) funded by the Ministry of Education,
4 Science and Technology (2013R1A1A2007365 and 2014R1A1A2055740).

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1 **Figure captions**

2 Fig. 1 Schematic diagram for the synthesis and morphology of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$
3 core-shell structure. Step (1): the surface functional groups (e.g., carbonyl, -hydroxyl,
4 carboxylic, etc) modification of graphite paper by electrochemical process. Step (2):
5 synthesis of the (Co, Mn)OOH on the graphite substrate by a hydrothermal method.
6 Step (3): phase transformation of (Co, Mn)OOH to MnCo_2O_4 nanowires onto the
7 graphite substrate and the formation of a carbon coating on the surface of the
8 MnCo_2O_4 nanowires during the thermal annealing process. Step (4): grafting of the
9 MnO_2 nanosheet to MnCo_2O_4 nanowires backbone by the second
10 hydrothermal method.

11 Fig. 2 (a) XRD of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ core-shell arrays on graphite paper. XPS
12 spectra of the $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ nanowires, (b) Mn 2p region, (c) Co 2p region.

13 Fig. 3 SEM images of (a-c) (Co, Mn)OOH. (d-f) MnCo_2O_4 nanowire arrays. (g-i)
14 $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ core-shell arrays.

15 Fig. 4 (a and b)TEM images of hierarchical mesoporous $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ core-shell.
16 (c) SAED pattern of the MnO_2 shell. (d) HRTEM image of MnCo_2O_4 core. (e)
17 Elemental mapping images of O, Co, and Mn.

18 Fig. 5 (a) Comparison of CV curves of the MnCo_2O_4 nanowire and $\text{MnCo}_2\text{O}_4@\text{MnO}_2$
19 electrodes and graphite paper at a current density of 10 mV s^{-1} . (b and c) CV curves
20 of the MnCo_2O_4 and $\text{MnCo}_2\text{O}_4@\text{MnO}_2$ electrodes at different scan rates. (d) Linear
21 relationship between the cathodic peak current and the square root of the scan rate.

22 Fig. 6 (a) Comparison of the CD curves of the MnCo_2O_4 and $\text{MnCo}_2\text{O}_4@\text{MnO}_2$
23 electrodes at a current density of 1 A g^{-1} . (b) Charge and discharge curves of the

1 MnCo₂O₄@MnO₂ electrode at different current densities. (c) Specific capacitances of
2 the as-synthesized electrode materials at different current densities. (d) Cycling
3 performance of the MnCo₂O₄ and MnCo₂O₄@MnO₂ electrodes at 10 A g⁻¹. (e)
4 Charge-discharge curves of the last 6 cycles of the MnCo₂O₄@MnO₂ electrode. (f)
5 CV curves of the MnCo₂O₄@MnO₂ electrode measured before and after 5000 cycles
6 charge-discharge test at 5 mV s⁻¹.

7 Fig. 7 (a and b) CV curves of the MnCo₂O₄@MnO₂//graphene/NF-ASC device at
8 different voltage windows and different scan rates, respectively. (c and d) CD curves
9 and specific capacitances of the ASC device at different current densities.

10 Fig. 8 (a) Schematic illustration of the ASC device configuration. (b) Cycling stability
11 of the MnCo₂O₄@MnO₂//graphene/NF-ASC device. (c) Ragone plot of the energy
12 density and power density at different current densities of the ASC device. (d) A
13 circuit diagram showing that two ASC devices connected in series can light up a red
14 LED indicator.

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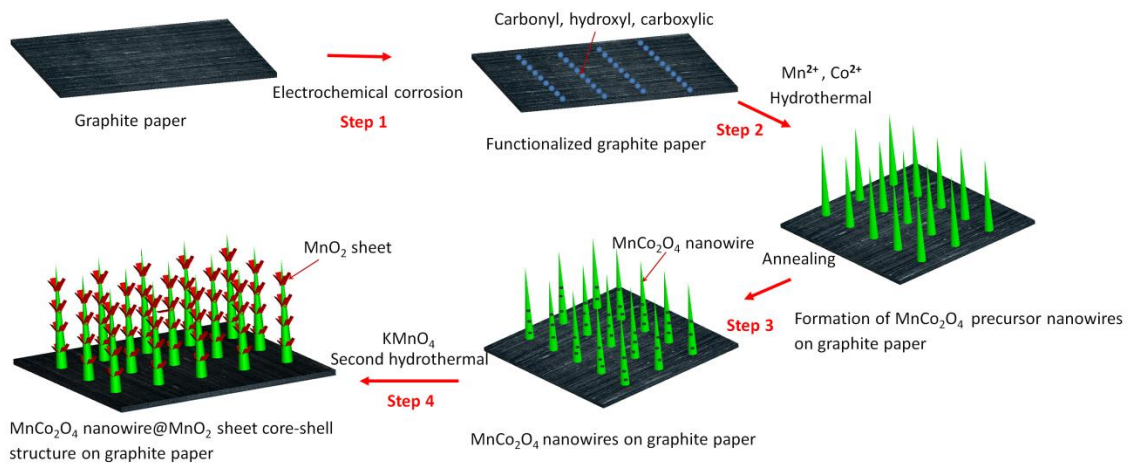
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Fig. 1

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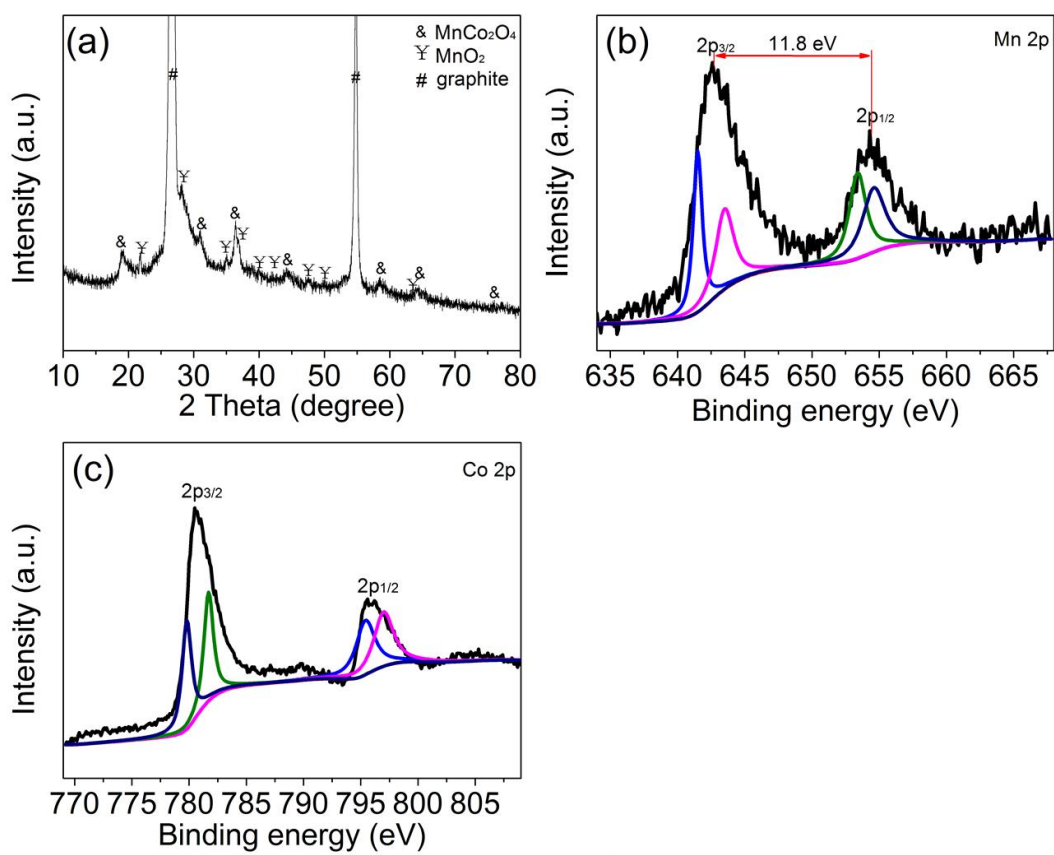
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Fig. 2

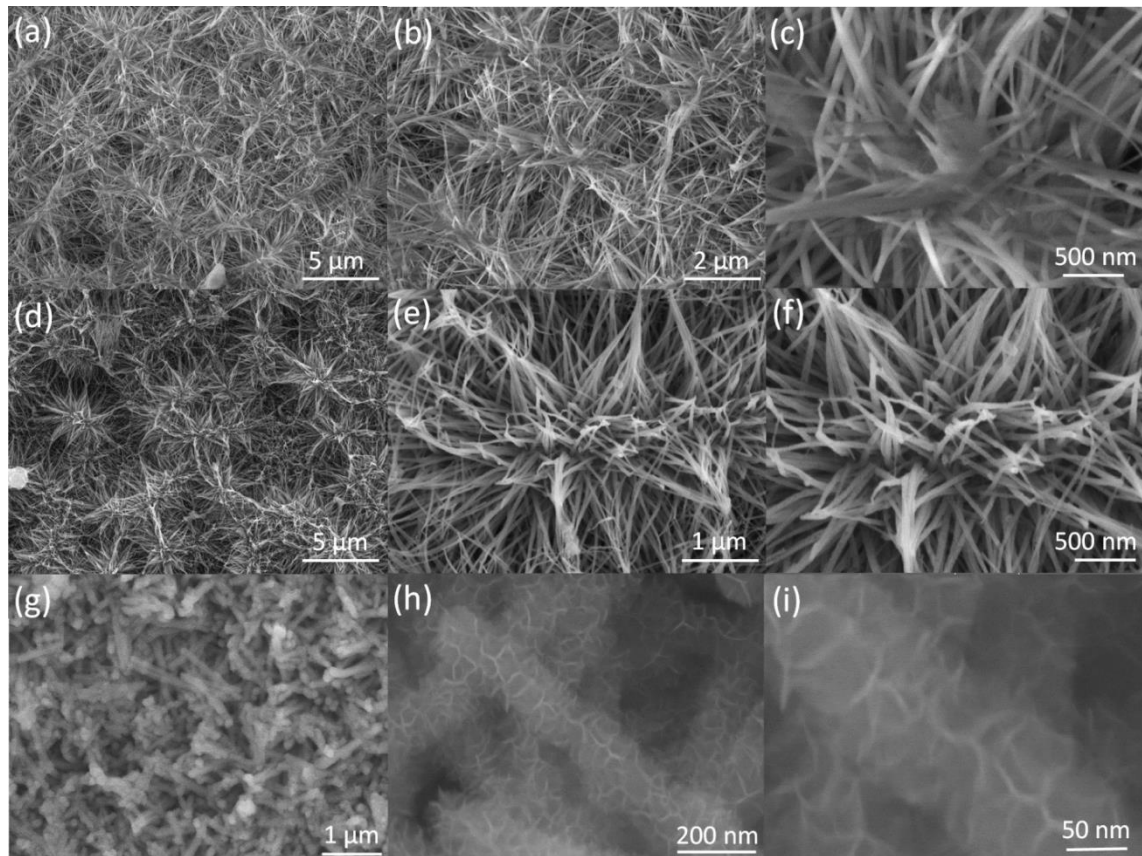


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Fig. 3

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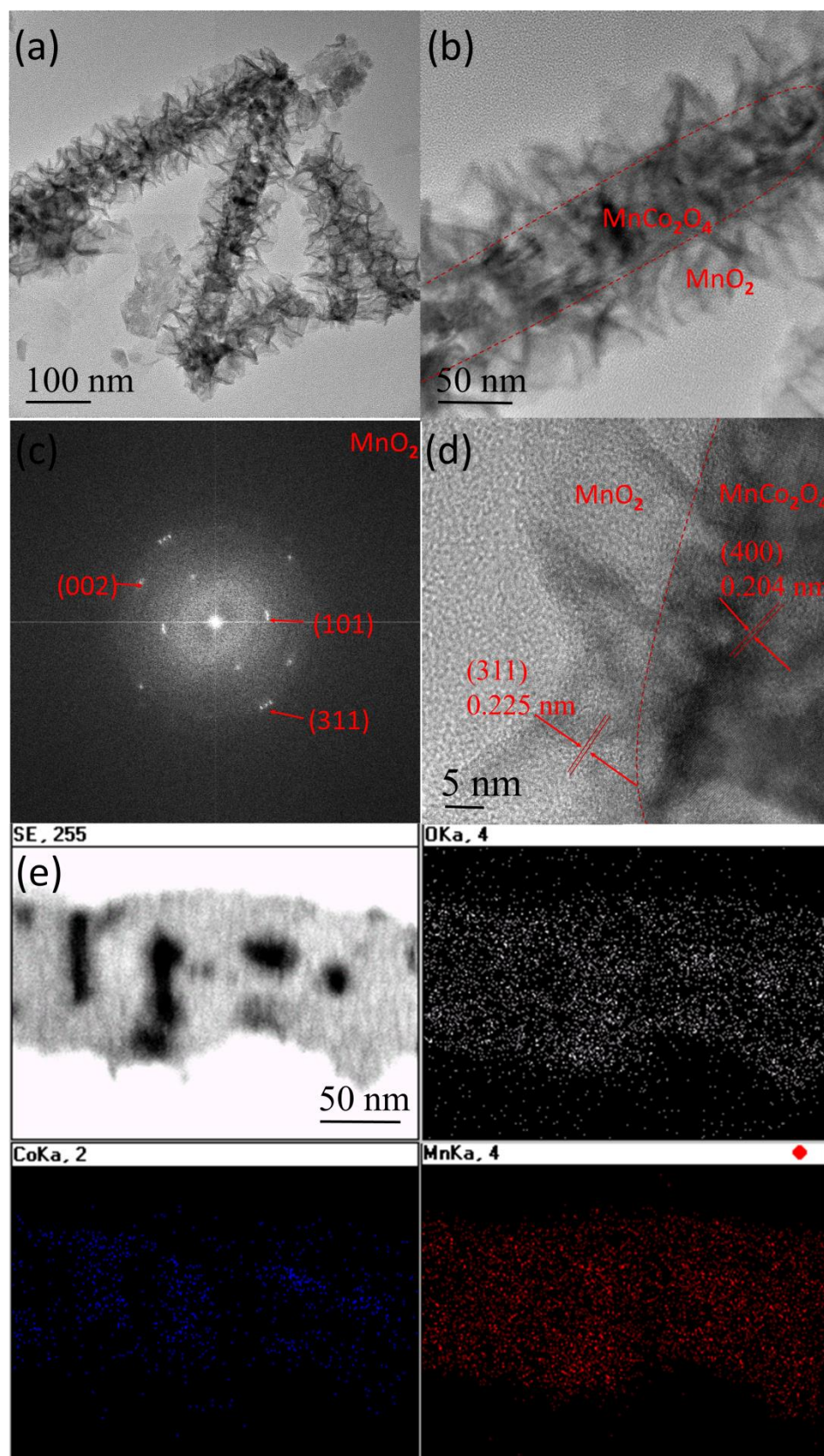
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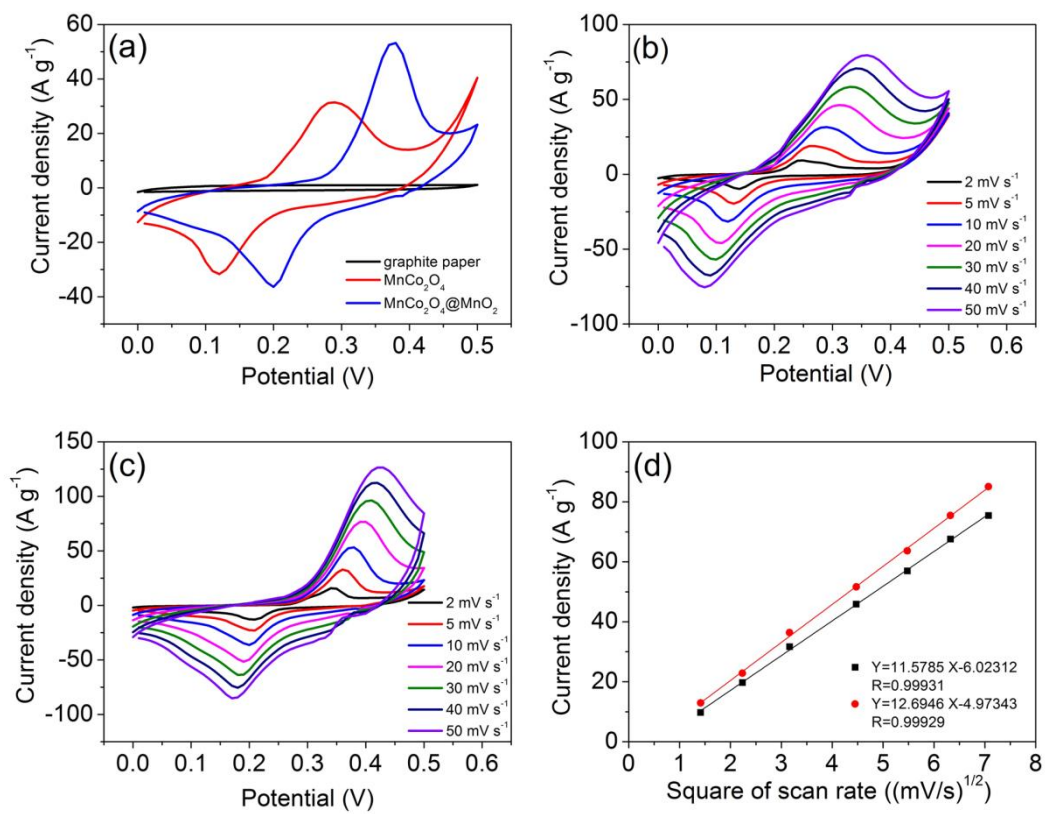
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Fig. 5

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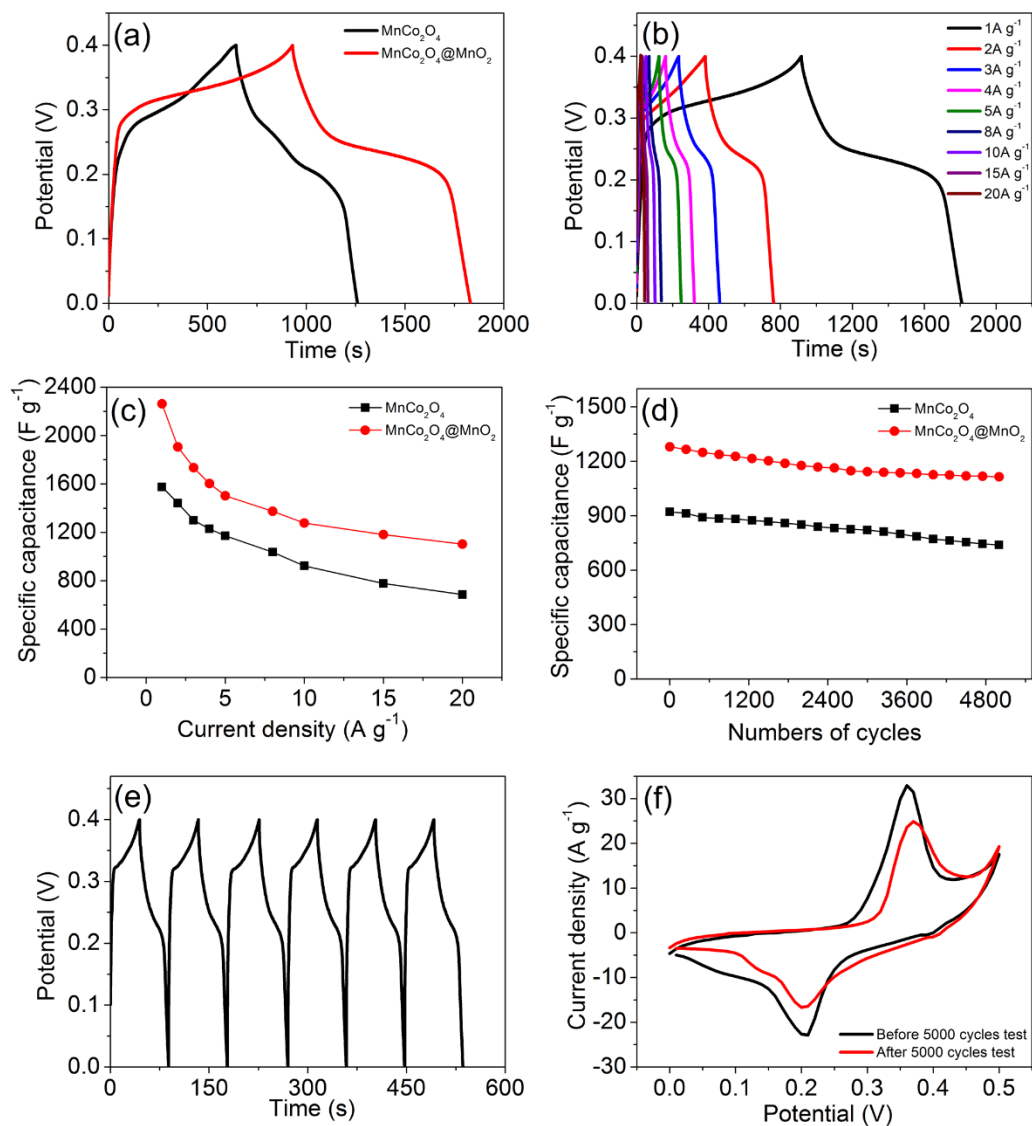
3

4

1

Fig. 6

2



3

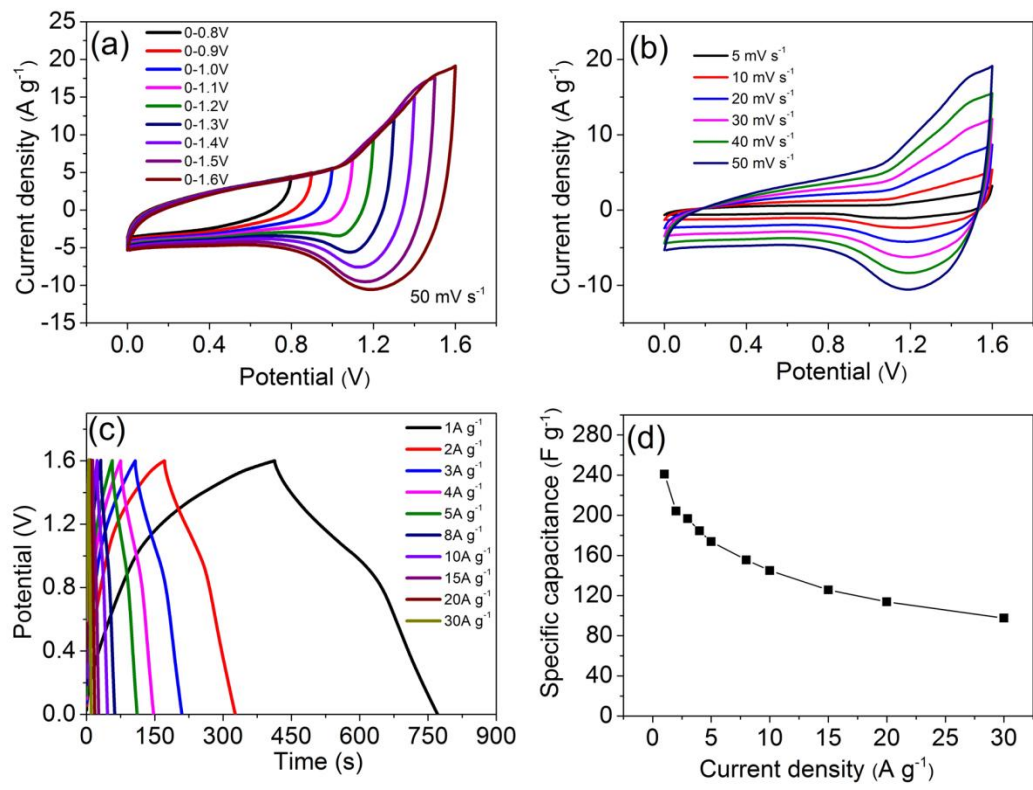
4

5

1

Fig. 7

2

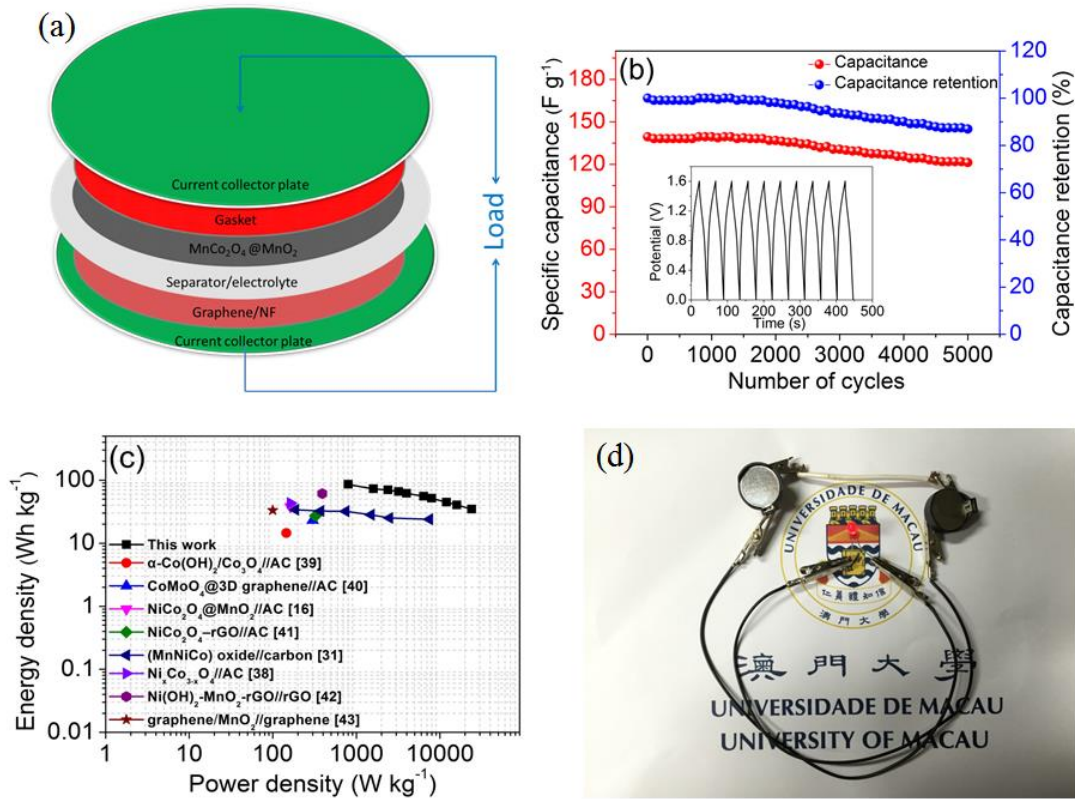


3

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Fig. 8

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