**Ultra-endurance flexible all-solid-state asymmetric
supercapacitors based on three-dimensionally coated MnO_x
nanosheets on nanoporous current collectors**

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Graphical abstract

Abstract

Three-dimensional (3D) porous current collector is effective in enhancing the energy density per surface area of batteries and supercapacitors due to its ability for high mass loading of active materials and efficient electron and ion transport. Herein, we report a facile method to construct a nanoporous Ni architecture on the surfaces of flexible carbon cloth (Ni@CC). By electrodeposition of ultrathin MnO_x nanosheets on the 3D Ni@CC nanoporous current collectors, we achieved an areal specific capacitance of 906.6 mF cm^{-2} at 1 mA cm^{-2} , which is much higher than 353.2 mF cm^{-2} using bare CC as the current collector. Employing the 3D MnO_x @Ni@CC positive electrode and a chemically converted graphene (CCG) negative electrode, we assembled a flexible all-solid-state asymmetric supercapacitor (AASC) in a Na_2SO_4 /polyvinyl alcohol (PVA) gel electrolyte. The AASC can achieve a superior energy density of $1.16 \text{ mW h cm}^{-3}$ at a current density of 1 mA cm^{-2} and excellent cyclability with 81.5% capacity retention after 10000 charging/discharging cycles. More importantly, the AASC can maintain over 85.7% of its original capacitance even after 200 bending cycles. These results demonstrate the great potential for application of 3D Ni@CC scaffolds in flexible, high performance wearable electronics and energy storage devices.

Keywords: Three-dimensional porous current collector; MnO_x @Ni hierarchical nanostructure; Flexible all-solid-state asymmetric supercapacitors; Energy storage devices.

1. Introduction

Flexible electrochemical energy storage devices attract much attention for their promising applications in the next generation portable and flexible electronics including roll up display, distributed sensors, and wearable multimedia computing [1-4]. The flexible all-solid-state asymmetric supercapacitor (AASC) is considered as one of most advanced flexible energy storage system due to its high power density, long cycle life, high safety, and comparable energy density to traditional batteries [5-8]. The mechanical properties and electrochemical performances of the electrode in a AASC are closely related to the properties of the flexible substrate (or current collector) [9-16]. Carbon cloth (CC) has been demonstrated to be a promising flexible current collector because of its high conductivity and robust mechanical strength [17-21]. Metal oxides/hydroxides [22-25] as well as conducting polymers [26] can be easily grown on flexible CC, avoiding the use of binder in the fabrication of AASC electrodes, which is beneficial for enhancing the cell's energy density. However, the limited surface area of CC impedes the further increase of active materials loading. As a result, the performance of current AASC is still far from meeting the requirement of practical applications. Therefore, an effective method is needed to modify the CC for significantly increasing its surface area.

Among different types of metal oxides, MnO_x has received the most attention because of its high theoretical specific pseudocapacitance ($> 1300 \text{ F g}^{-1}$), low cost, and environmental friendliness [27-30]. However, its poor intrinsic electrical

conductivity (10^{-5} - 10^{-6} S cm⁻¹) and low utilization rate limit its practical applications in supercapacitors [31-33]. Building nanostructure with desirable morphology and composition is of great importance for addressing this issue. For instance, Bao et al. developed a core@shell structure with ultrathin MnO₂ films coating on Zn₂SnO₄ nanowires grown on CC, which exhibited an improved electrochemical capacitive behavior [34]. Depositing ultrathin MnO₂ film on other metal oxide nanowires such as WO_{3-x} [9], H-TiO₂ [11], NiCo₂S₄ [35], and ZnO [36,37] also enhanced its electrochemical performance. Despite of the progress, the limited surface area of nanowires still leads to a relatively low loading of active materials. In addition, the performance of MnO₂ coated on nanowires degrades rapidly under bending conditions, probably due to the poor the interfacial contact [18-20]. Recently, three-dimensional (3D) porous structures [25-27] exhibit promising properties as scaffolds for loading active materials. The 3D porous network with high surface area and unique geometric structure not only increases mass loading of electroactive materials, but also ameliorates the transport of electrons and ions. However, most of the current 3D porous structures were constructed on non-flexible substrates, such as Ni foam [25], in which the void spaces cannot be efficiently used to deposit active materials. Therefore, it is necessary to develop a 3D porous network, especially on a flexible substrate, which can impart high specific surface area and high ionic permeability.

There are many works on the design and fabrication of supercapacitor electrode materials based on MnO_x coated metal, metal oxide and carbon nanomaterials to date. However, the exhibited performances of these electrodes with the freestanding and

flexible substrates are still unsatisfied, especially in term of volumetric energy density.

In this work, we designed a 3D porous Ni architecture on a flexible CC substrate (Ni@CC). The scaffold not only dramatically enhances the surface area of the substrate, and thus increases the loading of active materials; but also facilitates the electrolyte penetrating into active materials. MnO_x nanosheets as the active materials were electrodeposited on the 3D scaffold to form a 3D MnO_x@Ni@CC positive electrode. Chemically converted graphene (CCG) was used as the negative electrode due to its high specific capacitance of $> 200 \text{ F g}^{-1}$ and excellent rate capability [38]. We assembled flexible and light weight AASC using 3D MnO_x@Ni@CC and CCG in a Na₂SO₄/PVA gel electrolyte. The AASC could achieve a superior volumetric specific capacitance of 2.57 F cm^{-3} and a volumetric energy density of $1.16 \text{ mW h cm}^{-3}$ and excellent cyclability with 81.5% retention after 10000 charging/discharging cycles at a current densities of 2 mA cm^{-2} . The volumetric energy density is almost the highest values of CC-based supercapacitors. In addition, the AASC can also maintain above 85.7% of its original capacitance even after 200 bending cycles, well demonstrating its potential in flexible electronic applications.

2. Experimental Section

2.1 Chemicals

Carbon cloth (1 cm × 2 cm), nickel chloride hexahydrate puratrem (NiCl₂·6H₂O, 99%, Sigma-Aldrich), hexamethylenetetramine (HMT, C₆H₁₂N₄, 99%, Sinopharm Chemical Reagent Company Limited), graphite (C, powder, < 150 μm, Sigma-Aldrich),

hydrochloric acid (36.0-38.0 wt %, Sinopharm Chemical Reagent Company Limited), hydrazine hydrate solution ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 24-26% in water, Sigma-Aldrich), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt % in water, Aladdin), manganese sulfate (MnSO_4 , 99%, Sinopharm Chemical Reagent Company Limited), sodium acetate ($\text{C}_2\text{H}_3\text{O}_2\text{Na}$, 99%, Sinopharm Chemical Reagent Company Limited), polyvinyl alcohol (PVA, $[\text{CH}_2\text{CH}(\text{OH})]_n$, $n = 1799$, Aladdin) and sodium sulfate (Na_2SO_4 , 98%, Sinopharm Chemical Reagent Company Limited) were used directly without any further purification.

2.2 Growth of nanoporous Ni architecture on the surfaces of flexible CC

The as-purchased CC was ultrasonically cleaned in 5 M HCl aqueous solution, absolute ethanol and deionized (DI) water each for 15 min and then dried in air. **Then the clean CC was used as a substrate for depositing $\text{Ni}(\text{OH})_2$ after being cut into 1 cm $\times$ 2 cm pieces and protected by ethoxylane except an exposed area of 1 cm² on both sides.** Ni precursor solution was prepared by adding 0.125 mol of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.25 mol of HMT into 1 L distilled water. One piece of CC substrate with exposed area of 1 cm² was immersed into a 50 mL glass vessel with 30 ml Ni precursor solution; and then heated the vessel in an electric oven at 100 °C for 8 h to grow $\text{Ni}(\text{OH})_2$ on CC. Finally, the light green products grown on the CC were thoroughly rinsed with distilled water and ethanol several times, and then dried in vacuum oven overnight. To construct nanoporous Ni architecture on the surfaces of flexible CC, the as-obtained samples were heated under H_2/Ar mixed gas (5.0 vol % H_2) at 400 °C for 1 h with a heating rate of 5 °C min⁻¹.

2.3 Electrodeposition of MnO_x electroactive nanomaterials on 3D Ni@CC

To make MnO_x easily deposit on the surface of 3D Ni@CC, this 3D substrate was immersed into 0.5 M HCl aqueous solution for pretreating 1-2 min. Then, an electrodeposition process was performed in a standard three electrode glass cell, with this 3D Ni@CC substrate as the working electrodes, a saturated calomel electrode (SCE) as the reference electrode, and platinum foil as the counter electrode. The electrolyte contained 0.5 M Mn(CH₃COO)₂, 0.5 M Na₂SO₄ and 50 mL 10% ethanol. Anodic pulses (0.7-1.4 V; 1s on, 5s off) were applied to deposit MnO_x on the electrode. The weight of MnO_x in MnO_x@Ni@CC electrode was calculated by weighing before and after the 3D@Ni@CC loading MnO_x (Mettler Toledo XP26, resolution of 1 µg).

2.4 Preparation of CCG electrode

CCG was prepared according to the method reported by our previous work [38]. In a brief synthesis process, 30 mL graphene oxide solution (0.05 wt % in water) mixed with 210 µL hydrazine solution (35 wt % in water) and 210 µL ammonia solution (28 wt % in water) in a 50 mL glass vessel. Then the vessel was heated at 100 °C for 3 h to obtain CCG dispersion. The CCG hydrogel films were obtained by vacuum filtrating the as-obtained CCG dispersion through a mixed cellulose ester filter membrane (0.05 µm pore size). Noted that the vacuum should be disconnected immediately once no free CCG dispersion was left on the filter cake and the peeled off CCG hydrogel film from the filter membrane should be immediately transferred into a Petri dish filled with DI water to guarantee the quality of the as-obtained film.

The remaining ammonia and hydrazine in CCG hydrogel film were removed through immersing the film into DI water for overnight. In this work, the thickness of CCG film used as negative electrode is around 10 μm evaluated from SEM images shown in Fig. S1. The weight of CCG as negative electrode was also determined by weighting.

2.5 Assembling AASCs

The gel electrolyte was prepared by mixing 6 g Na_2SO_4 and 6 g PVA in 60 mL DI water under vigorous stirring at 80 $^{\circ}\text{C}$ for 1 h. The as-prepared CCG was cut into rectangular strips with a dried weight of ~ 3.0 mg and then pressed on the gold coated polyimide substrate (surface resistance about 2 Ω) under a pressure of ~ 1 MPa to form a thin film with a thickness of ~ 10 μm and areal mass of ~ 3.0 mg cm^{-2} . The as-fabricated 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode and CCG pressed on gold coated polyimide substrate were immersed into the $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte for 60 min, and subsequently maintained at 80 $^{\circ}\text{C}$ overnight to evaporate the excess of water in the electrolyte. The AASCs were assembled by pressing these two electrodes with gel electrolyte together under a pressure of ~ 1 MPa for 10 min, which can facilitate the polymer gel electrolyte penetrating into each electrode and also form one thin separator layer.

2.6 Electrochemical measurements

All electrochemical performances of the samples were measured by a CHI 660C electrochemical workstation (CH Instruments Inc.). In half cell tests, the electrochemical measurements were performed in a standard three electrode glass cell

at room temperature with 1 M Na₂SO₄ aqueous solution as the electrolyte; MnO_x deposited on 3D Ni@CC or bare CC as the working electrode; Ag/AgCl electrode as the reference electrode and a platinum foil as the counter electrode. In full cell tests, the MnO_x@Ni@CC // CCG AASCs were used to evaluate the electrochemical performance.

2.7 Characterization

The microstructure of the samples were characterized using a Quanta 400 FEG scanning electron microscope (SEM) and a Tecnai G2 F20 S-Twin transmission electron microscope (TEM). X-ray diffraction (XRD) was used to study the crystal structure of the samples with a Bruker D8 diffractometer; X-ray photoelectron spectroscopy (XPS) characterization was performed on an Axis Ultra DLD X-ray photoelectron spectroscopy. Raman spectra were also used to analyze the structure information of the as-obtained samples with a LabRAM HR evolution Raman spectrometer.

3. Results and Discussion

Fig. 1. (a) Schematic process of MnO_x active materials depositing on a 3D Ni@CC, (b) SEM image of Ni(OH)₂ nanosheets deposited on CC, (c) SEM image of the as-obtained 3D Ni@CC, (d) SEM images of 3D MnO_x@Ni@CC. The inset of (b-d) show high magnification SEM image of Ni(OH)₂@CC, 3D Ni@CC, 3D MnO_x@Ni@CC, respectively.

Our strategy for fabricating 3D MnO_x@Ni@CC electrode involves three steps: firstly, coating a layer of Ni(OH)₂ nanosheets on bare CC through the reaction of HMT and NiCl₂·6H₂O; then reducing Ni(OH)₂ into Ni to form 3D Ni@CC under H₂/Ar mixed gas; and finally controllable electrodeposition of MnO_x nanosheets on the surface of Ni@CC to form MnO_x@Ni@CC (Fig. 1a). The microstructure of the as-obtained

samples in each step was characterized by SEM. As shown in Fig. 1b, it can be found that $\text{Ni}(\text{OH})_2$ nanosheets were homogeneously grown on the surface of CC and the thickness of these nanosheets is around 20 nm. The as-formed $\text{Ni}(\text{OH})_2$ nanosheets can be confirmed by XRD pattern (Fig. S2a), and all diffraction peaks are well consistent with the rhombohedral $\alpha\text{-Ni}(\text{OH})_2$ (JCPDS card no. 38-0715) [39-41]. As shown in Fig. 1c, porous Ni nanonet can be formed from the reduced $\text{Ni}(\text{OH})_2$ nanosheets. High magnification SEM result further reveals that the porous Ni nanonet is composed of the interconnected Ni nanoparticles with size of ~ 50 nm (Fig. 1c inset and Fig. S3). XRD results in Fig. S2b confirm that $\text{Ni}(\text{OH})_2$ were successfully reduced into Ni, in which all peaks match well with the standard Ni peaks (JCPDS 04-0850). TEM is also used to study the detailed microstructure of the as-obtained nanoporous Ni@CC current collectors. Fig. 2a shows the formed Ni nanoparticles are interconnected, which is well consistent with SEM results shown in Fig. 1c. A typical high resolution TEM (HRTEM) image (Fig. 2b) discloses the fine structure of the Ni. The lattice fringes with a spacing of 0.203 nm is consist with the spacing of the (111) plane of Ni.

Fig. 2. (a, b) TEM and HRTEM image of the porous Ni nanonet; (c, d) TEM images, (e) EDX pattern, and (f, g) Ni and Mn mapping of the porous Ni nanonet coated with a thin layer of MnO_x nanosheets. **The inset of (d) shows a HRTEM image of MnO_x nanosheets.**

Considering the unique structure and excellent conductivity of porous Ni nanonets, 3D Ni@CC should be a promising substrate for depositing active materials. In this work, MnO_x was electrodeposited on this 3D Ni@CC substrate. Fig. 1d shows that

the electrodeposited MnO_x nanosheets completely cover on the surface of Ni nanonets. More details about the 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ structure were investigated by TEM. As shown in Fig. 2c and Fig. 2d, it can be found that the Ni nanonets are uniformly wrapped by numerous MnO_x nanosheets and these nanosheets are very thin with the thickness of around several nanometers. A HRTEM image (inset of Fig. 2d) displays the lattice spacing of 0.248 nm and 0.281 nm, well matching up with the inter-planar spacing of (211) and (103) planes of tetragonal Mn_3O_4 , which is consistent with the XRD results (Fig. S5). Energy dispersive X-ray spectroscopy (EDS) results in Fig. 2e confirms the existence of Mn and Ni elements in the as-obtained samples and the weight ratio of MnO_x was estimated to be 31.2 wt % in the $\text{MnO}_x@\text{Ni}$ composite. It should be noted that the detected Cu element is from the Cu grid. From the elemental mapping results, it can clearly observe the hierarchical core-shell nanostructure of $\text{MnO}_x@\text{Ni}$ (Fig. 2f, 2g). For a comparison, bare CC substrate was also used to electrodeposit MnO_x . As shown in Fig. S4, it can be found that a thin layer of MnO_x nanosheets grown on the surface of CC. However, with the absence of Ni porous nanonet, the loading of MnO_x nanosheets on CC is much lower than that on 3D $\text{Ni}@\text{CC}$.

Fig. 3. (a, b) XPS and Raman spectrum of MnO_x deposited on 3D Ni@CC.

The high resolution XPS and Raman scattering spectrum were used to further study the chemical composition of MnO_x . Typical XPS spectrum of Mn2p and O1s for MnO_x electrodeposited on 3D Ni@CC at 900 s are shown in Fig. 3a. The Mn $2p_{3/2}$ and Mn $2p_{1/2}$ binding energy are centered at 642.3 eV and 654.1 eV, respectively, and the difference between Mn $2p_{3/2}$ peak and $2p_{1/2}$ peak is about 11.8 eV. It can be evaluated that the average oxidation state of Mn in the MnO_x nanosheets is around 3.6 [17, 42]. All these results well reveal the co-existence of both Mn^{4+} and Mn^{3+} ions in the as-synthesized samples. On the other hand, the peaks at 529.8, 531.5, and 532.7 eV in the O1s spectrum can be attributed to Mn-O-Mn, Mn-OH and H-O-H, respectively, suggesting that the as-electrodeposited MnO_x nanosheets are composed of MnO_2 , Mn_3O_4 and MnOOH [43-45]. Some results found that alkaline or proton ions can migrate in the lattice of manganese oxide by hopping between the H-O-H and OH^- sites [46]; the more H-O-H and OH^- hopping sites, the faster ion transport [47]. Considering abundant H-O-H groups in our samples, the ion conductivity of the as-obtained MnO_x must be dramatically enhanced, which will benefit the rate

capability during charging and discharging. In Raman spectrum, one sharp peak at 655 cm^{-1} and one broad peak from 255 to 410 cm^{-1} can be observed (Fig. 3b). The peak at 655 cm^{-1} corresponds to the Mn-O breathing vibration of divalent Mn ions in tetrahedral coordination, and the broad peak may be attributed to the overlap of various characteristic peaks from MnO_2 , Mn_3O_4 and MnOOH [48-49], which is well consistent with XPS results. As shown by these analytical results (HRTEM, XRD, XPS and Raman spectrum), the as-electrodeposited MnO_x nanosheets are composed of MnO_2 , Mn_3O_4 and MnOOH ; moreover, the abundant OH groups in MnO_x will dramatically accelerate the ion transport rate during charging and discharging, and thus enhance the rate capability.

Fig. 4. (a) Comparisons of CV curves of the 3D MnO_x@Ni@CC electrode obtained at different deposition times at a scan rate of 20 mV s⁻¹, (b) calculated areal specific capacitances of 3D MnO_x@Ni@CC and MnO_x@CC electrodes under the different deposition times, (c, e) CV curves and galvanostatic charge/discharge curves of the 3D Ni@CC electrode at the deposition time of 900 s at various scan rates and current densities, (d, f) areal and mass specific capacitances of 3D MnO_x@Ni@CC and MnO_x@CC electrodes as a function of

various scan rates and current densities.

The electrochemical properties of this unique 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ were firstly evaluated by cyclic voltammetry (CV) with a standard three electrode configuration containing 1 M NaSO_4 electrolyte at room temperature. Fig. 4a shows CV curves of the 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ electrodes with different MnO_x deposition times ranging from 60 to 1080 s in the voltage range of 0-0.8 V at a scan rate of 20 mV s^{-1} . It can be observed that there is a pair of redox peaks in each CV curves, indicating that the capacitance comes from the combination of both electrochemical double-layer capacitance and pseudocapacitance generated by faradic redox reactions of Mn^{4+} and Mn^{3+} ions [50-53]. The redox peaks can be attributed to the $\text{Mn(III)} \rightleftharpoons \text{Mn(IV)} + \text{e}^-$, and the mixed-valence Mn ions were confirmed by the aforementioned discussion. Note that the 3D $\text{Ni}@\text{CC}$ electrode without the active MnO_x material shows almost negligible capacitance (Fig. S6), indicating Ni will not contribute capacitance in $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode. From CV curves, the areal specific capacitance can be calculated based on $C_a = A/2v\Delta V S$ (The detailed calculation can be found in supporting information). As shown in Fig. 4b, it can be found that the areal specific capacitances initially increases with the MnO_x deposition times for both $\text{MnO}_x@\text{Ni}@\text{CC}$ and $\text{MnO}_x@\text{CC}$ electrodes; and then it reduces slightly after reaching its peak value. The highest areal specific capacitance for $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode is around 726.5 mF cm^{-2} , corresponding to a deposition time of 900 s and MnO_x mass of 0.728 mg cm^{-2} . It is worth pointing out that such mass loading of

MnO_x is much higher than those of recently reported CC-based electrodes, such as MnO₂@H-TiO₂@CC electrode (0.19-0.23 mg cm⁻²) [11], and MnO₂@ZnO@CC electrode (0.50 mg cm⁻²) [60] (Table. S1). In contrast, the peak areal specific capacitance for MnO_x@CC electrode is only 212.92 mF cm⁻², corresponding to a deposition time of 600 s and MnO_x mass of 0.485 mg cm⁻². It can be calculated that the 3D Ni@CC substrate can load 1.5 times more MnO_x mass than bare CC substrate, indicating a much larger surface area of 3D Ni@CC substrate. The decreasing areal specific capacitance behavior for too long deposition time, such as 1080 s corresponding to an areal specific capacitance of 705.7 mF cm⁻², reveals that too much MnO_x deteriorates the electrochemical properties.

Based on the above experiments results, it can be concluded that the optimized electrodeposition time is 900 s for 3D MnO_x@Ni@CC electrodes, the correspondingly optimized electrode will be used in the following electrochemical study. As shown in Fig. 4c, the 3D MnO_x@Ni@CC electrode was further investigated over a range of CV scan rates of 5-100 mV s⁻¹. The CV curves with almost rectangular shape again demonstrate the excellent charge storage characteristics and ultrafast response of the MnO_x@Ni@CC electrode [54,55]. The areal specific capacitance at different scan rate was calculated and plotted in Fig. 4d. At scan rates of 5, 10, 20, 50, 100 mV s⁻¹, the corresponding areal specific capacitances are 888.56 (1220.9), 810.3 (1113.4), 734.2 (1009.2), 661.6 (909.6) and 594.9 mF cm⁻² (816.7 F g⁻¹), respectively. It should be noted that even at a higher scan rate of 100 mV s⁻¹, the 3D MnO_x@Ni@CC electrode can still deliver a relatively high areal specific

capacitance of 594.9 mF cm^{-2} , indicating its high rate performance. In contrast, the areal specific capacitances of $\text{MnO}_x@\text{CC}$ electrode with the same mass loading are only 302.3 mF cm^{-2} (415.25 F g^{-1}) and 113.8 mF cm^{-2} (156.32 F g^{-1}) at scan rates of 5 mV s^{-1} and 100 mV s^{-1} , respectively, much lower than the values delivered by 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode, well demonstrating the advantage of our engineered 3D nanoporous $\text{Ni}@\text{CC}$ current collectors.

The galvanostatic charge/discharge curves of $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode are shown in Fig. 4e at different current densities. The deviation from the ideal triangle shape confirms the significant contribution of pseudocapacitance. The areal specific capacitances were derived from the galvanostatic charge/discharge curves are shown in Fig. 4f. The 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode delivers an impressive areal specific capacitance of 906.6 mF cm^{-2} at a current density of 1.0 mA cm^{-2} , more than 2.8 times higher than that of $\text{MnO}_x@\text{CC}$ electrode (321.3 mF cm^{-2}) (Fig. S7). Furthermore, upon increasing the current density up to 40 mA cm^{-2} , the areal specific capacitance of 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode remains at 162.8 mF cm^{-2} , more than 3 times higher than that of 3D $\text{MnO}_x@\text{CC}$ electrode (52.1 mF cm^{-2}), suggesting the excellent rate capability of 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ electrode. The measured areal specific capacitance depends strongly on current density for high mass loading electrodes; while depends weakly on current density for low mass loading electrodes (Fig. S8). For example, the areal specific capacitance decreases from 867.3 mF cm^{-2} at 1.0 mA cm^{-2} to 72.7 mF cm^{-2} at 40 mA cm^{-2} for the 1080 s electrodeposition electrode (the capacitance retention is 8.4%). In comparison, it decreases from 87.8 mF cm^{-2} at 1.0 mA cm^{-2} to

69.5 mF cm⁻² at 40 mA cm⁻² for the 60 s electrodeposition electrode (the capacitance retention is 79%). This is mainly due to the limited conductivity of high mass loading samples and the limited utilization of MnO_x at higher current density [12]. Correspondingly, the mass specific capacitance of 3D MnO_x@Ni@CC electrode is also much superior to that of MnO_x@CC electrode. For instance, the peak mass specific capacitance of 3D MnO_x@Ni@CC electrode is around 1241.3 F g⁻¹, almost identical to the theoretical value 1370 F g⁻¹, much higher than 452.6 F g⁻¹ delivered by MnO_x@CC electrode. The significantly improved performance can be ascribed to the highly accessible surface area and increased electrical conductivity of the engineered 3D Ni@CC nanoporous current collectors.

In order to demonstrate the superior performances of 3D MnO_x@Ni@CC electrodes for electrochemical energy storage in flexible electronics, we further fabricated flexible AASC based on 3D MnO_x@Ni@CC as positive electrode and CCG as the negative electrode (denoted as MnO_x@Ni@CC // CCG). CCG hydrogel films were selected as flexible negative electrode due to its large capacitance at the ultrahigh current density, excellent rate capability and exceptional mechanical property [56,57]. Before evaluating the AASC performances, CV test for 3D MnO_x@Ni@CC and CCG were individually performed at a scan rate of 100 mV s⁻¹. As shown in Fig. S5, the stable potential window range for 3D MnO_x@Ni@CC is 0-0.8 V, while for CCG is -1-0 V; therefore, it is expected that the operating voltage potential can be extended to 1.8 V for MnO_x@Ni@CC // CCG flexible AASC. As well known, a balanced positive electrode and negative electrode can achieve the

maximum performance for an AASC device. In our device, it has been evaluated that the area ratio between 3D $\text{MnO}_x\text{@Ni@CC}$ electrode and CCG electrode is around 1 (the calculation detail can be found in the supporting information).

Fig. 5. (a, b) CV and galvanostatic charge/discharge curves of the AASC at various scan rates and current densities, (c) corresponding volumetric specific capacitance as a function of current densities and the inset is the schematic illustration of the

structure of our AASC, (d) IR drop as a function of current densities, (e) energy density as a function of power density, (f) cycling stability of the AASC over 10000 cycles at 2 mA cm^{-2} and the inset is the device can lighten up a red LED indicator (1.8 V).

The CV curves of the $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ flexible AASC are shown in Fig. 5a with the voltage window of 0-1.8 V at scan rates of 2-200 mV s^{-1} . All CV curves exhibit rectangular shapes without obvious redox peaks, even at a high scan rate of 200 mV s^{-1} , suggesting good reaction reversibility and typical capacitive characteristics of our device. Additionally, all the galvanostatic charge/discharge curves at various current densities in the voltage range of 0-1.8 V show triangular shapes, further demonstrating good capacitive behavior and fast galvanostatic charge/discharge behavior of the device (Fig. 5b). The volumetric capacitance of $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ flexible AASC were calculated from galvanostatic charge/discharge measurements. As shown in Fig. 5c, it can be found that the volumetric specific capacitances are 2.57, 2.15, 1.93, 1.84, 1.78 and 1.70 F cm^{-3} , at current densities of 1, 2, 4, 8, 10 and 20 mA cm^{-2} , respectively. The peak volumetric specific capacitance of 2.57 F cm^{-3} is much higher than that the previously reported values for $\text{Au}@\text{MnO}_x // \text{CCG}$ AASC (1.36 F cm^{-3}) [22] and $\text{MnO}_2 // \text{Fe}_2\text{O}_3$ AASC (1.5 F cm^{-3}) (Table. S1) [58].

As well known, the internal resistance has a significant influence on the performance of a device. By plotting the values of initial voltage drop as a function of current density, the internal resistance of our $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ flexible AASC

can be expressed by the following equation: IR drop (V) = 0.00023 + 0.01117 I (Fig. 5d). It indicates that our device has a very small internal resistance, which will be beneficial for high discharge power delivery in practical applications. To further interpret the benefit, the electrochemical impedance spectroscopy (EIS) measurement result was shown in Fig. S10 and the equivalent circuit was present in the inset of Fig. S10. The equivalent circuit consisting of the equivalent series resistance (R_s), charge-transfer resistance (R_{ct}), double layer capacitance (C_{DL}), pseudocapacitance (C_{PS}) and Warburg behaviour (W). At high frequency range, the value of the intercept at the real axis is used to estimate the R_s of the device, which is the combination of the contact resistance between electrode material and conductive substrate, the bulk solution resistance of the electrolyte, and the resistance of the electrode material itself. The R_s value for the $MnO_x@Ni@CC // CCG$ AASC is only 4.9 Ω , which is well consistent with internal resistance analysis. A comparison of the power and energy density of our AASC with various reported MnO_x based AASCs is given in Fig. 5e. Evidently, the performance of our $MnO_x@Ni@CC // CCG$ flexible AASC is superior to most contemporary devices. The $MnO_x@Ni@CC // CCG$ flexible AASC delivers the high energy density of 1.16 mW h cm⁻³ at a power density of 0.021 W cm⁻³ for CC-based AASCs (Table. S1), much higher than the values of $MnO_2@ZnO // RGO$ (0.234 mW h cm⁻³) [59], $MnO_2 // RGO$ (0.25 mW h cm⁻³) [60], $MnO_2@H-TiO_2 // C@H-TiO_2$ (0.3 mW h cm⁻³) [11], $MnO_2 // Fe_2O_3$ (0.55 mW h cm⁻³) [61], $MnO_2 // Ti-Fe_2O_3@PEDOT$ (0.89 mW h cm⁻³) [10], and $MnO_2 @graphene // VOS@C$ (0.87 mWh cm⁻³) [9].

For practical application, the cycle life and capacitance retention of the device are

important factors. The cycling test over 10000 cycles for $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ electrodes in $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte at the current densities of 2 mA cm^{-2} was conducted, as shown in Fig. 5f. Approximately 81% retention in capacitance over 10000 cycles and coulombic efficiencies of the electrode more than 99% were measured for the device, indicating an excellent stability and efficacy of the rapid electron transfer during charge/discharge processes. After charging, the $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ flexible AASC can light up a red light emitting diode (LED) indicator, demonstrating its practical applications (inset of Fig. 5f).

Fig. 6. (a) Four digital pictures show the flexibility of the $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ AASC when bended, (b) CV curves of the AASC under different bending conditions, (c) Capacitance retention of different bending conditions.

To investigate the mechanical flexibility of the $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ device, bending test was performed. As shown in Fig. 6a, the device keeps its structural

integrity upon bending inward to angle of 90°, 135° and 180°, indicating the robust mechanical property of the device. The influence of the bending induced mechanical stress upon the specific capacitance was also studied. Fig. 6b shows CV measured at a scan rate of 50 mV s⁻¹ for the MnO_x@Ni@CC // CCG flexible AASC under different bending angles and different bending cycles. It can be found that the flexible AASC exhibits minimal change in the charge/discharge behavior upon bending to different angles. Correspondingly, the change of the capacitance with increasing bending angle (0-180°) is also negligible, less than 5% (Fig. 6c). Furthermore, the effect of bending cycles for 180° bending was also investigated. As shown in Fig. 6c, the capacitance can still remain 85.7% even after bending 200 cycles. These findings well demonstrate that extensive and repetitive bending has a negligible impact on the capacitive performance of our device. The microstructure of this 3D MnO_x@Ni@CC electrode after bending 200 cycles was shown in Fig. S11. It can be observed that the structure of electrode remains unchanged, indicating the robust mechanical property of this unique 3D MnO_x@Ni@CC electrode, which contributes to the excellent capacitance retention under various bending conditions.

4. Conclusions

In summary, we reported a facile method for constructing a 3D nanoporous Ni architecture on flexible CC. Using this unique 3D Ni@CC as the substrate, the deposited MnO_x nanosheets deliver a superior areal specific capacitance of 906.6 mF

cm^{-2} at 1.0 mA cm^{-2} . Furthermore, a flexible and lightweight AASC is designed based on this 3D $\text{MnO}_x@\text{Ni}@\text{CC}$ as the positive electrode and CCG as the negative electrode in $\text{Na}_2\text{SO}_4/\text{PVA}$ gel electrolyte. The $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ flexible AASC exhibits excellent performance with energy density of $1.16 \text{ mW h cm}^{-3}$ at 1 mA cm^{-2} , 81.5% capacitance retention after 10000 charging/discharging at 2 mA cm^{-2} and 85.7% capacitance retention after 200 bending cycles. These results well demonstrate that our $\text{MnO}_x@\text{Ni}@\text{CC} // \text{CCG}$ flexible AASC is a promising candidate for future applications in flexible modern electronic devices.

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References

- [1] M.F. El-Kady, V. Strong, S. Dubin, R.B. Kaner, Science. 335 (2012) 1326-1330.
- [2] Y. Qin, X. Wang, Z. Wang, Nature, 451 (2008) 809-813.

- [3] X. Lu, M. Yu, G. Wang, Y. Tong, Y. Li, *Energy Environ. Sci.* 7 (2014) 2160-2181.
- [4] M.F. El-Kady, R.B. Kaner, *Nat. Commun.* 4 (2013) 1475-1475.
- [5] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845-854.
- [6] P.J. Hall, M. Mirzaeian, S.I. Fletcher, F.B. Sillars, A.J.R. Rennie, G.O. Shitta-Bey, G. Wilson, A. Cruden, R. Carter, *Energy Environ. Sci.* 3 (2010) 1238-1251.
- [7] E. Frackowiak, *Phys. Chem. Chem. Phys.* 9 (2007) 1774-1785.
- [8] Y. Qiu, G. Li, Y. Hou, Z. Pan, H. Li, W. Li, M. Liu, F. Ye, X. Yang, Y. Zhang, *Chem.Mater.* 27 (2015) 1194-1200.
- [9] T. Zhai, X. Lu, Y. Ling, M. Yu, G. Wang, T. Liu, C. Liang, Y. Tong, Y. Li, *Adv. Mater.* 26 (2014) 5869-5875.
- [10] Y. Zeng, Y. Han, Y. Zhao, Y. Zeng, M. Yu, Y. Liu, H. Tang, Y. Tong, X. Lu, *Adv. Energy. Mater.* 5 (2015) 1402176.
- [11] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong, Y. Li, *Adv. Mater.* 25 (2013) 267-272.
- [12] W. Chen, R.B. Rakhi, L. Hu, X. Xie, Y. Cui, H.N. Alshareef, *Nano Lett.* 11 (2011) 5165-5172.
- [13] J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen, G. Shen, *ACS Nano.* 7 (2013) 5453-5462.
- [14] P.C. Chen, G. Shen, Y. Shi, H. Chen, C. Zhou, *ACS Nano.* 4 (2010) 4403-4411.
- [15] H.-P. Cong, X.-C. Ren, P. Wang, S.-H. Yu, *Energy Environ. Sci.* 6 (2013) 1185-1191.
- [16] Y. Jin, H. Chen, M. Chen, N. Liu, Q. Li, *ACS Appl. Mater. Interfaces.* 5 (2013)

3408-3416.

[17] X. Xia, Y. Zhang, D. Chao, Q. Xiong, Z. Fan, X. Tong, J. Tu, H. Zhang, H. Fan, *Energy Environ. Sci.* 8 (2015) 1559-1568.

[18] X. Lang, A. Hirata, T. Fujita, M. Chen, *Nat. Nanotechnol.* 6 (2011) 232-236.

[19] G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui, Z. Bao, *Nano Lett.* 11 (2011) 4438-4442.

[20] X. Lu, G. Wang, T. Zhai, M. Yu, S. Xie, Y. Ling, C. Liang, Y. Tong, Y. Li, *Nano Lett.* 12 (2012) 5376-5381.

[21] N. Yu, M. Zhu, D. Chen, *J. Mater. Chem. A.* 3 (2015) 7910-7918.

[22] G. Wang, X. Lu, Y. Ling, T. Zhai, H. Wang, Y. Tong, Y. Li, *ACS Nano.* 6 (2012) 10296-10302.

[23] Y. Zeng, Y. Han, Y. Zhao, Y. Zeng, M. Yu, Y. Liu, H. Tang, Y. Tong, X. Lu, *Adv. Energy Mater.* 5 (2015) 1402176.

[24] X. Xiao, T. Ding, L. Yuan, Y. Shen, Q. Zhong, X. Zhang, Y. Cao, B. Hu, T. Zhai, J. Zhou, Z. Wang, *Adv. Energy Mater.* 2 (2012) 1328-1332

[25] J. Li, J. Xiao, Z. Wang, Z. Wei, Y. Qiu, S. Yang, *Nano Energy.* 10 (2014) 329-336.

[26] Z. Niu, P. Luan, Q. Shao, H. Dong, J. Li, J. Chen, D. Zhao, L. Cai, W. Zhou, X. Chen, S. Xie, *Energy Environ. Sci.* 5 (2012) 8726-8733.

[27] J. Xiao, S. Yang, L. Wan, F. Xiao, S. Wang, *J. Power. Sources.* 245 (2014) 1027-1034.

[28] Z. Yu, B. Duong, D. Abbitt, J. Thomas, *Adv. Mater.* 25 (2013) 3301-3301.

[29] Z. Zhang, F. Xiao, L. Qian, J. Xiao, S. Wang, Y. Liu, *Adv. Energy Mater.* 4 (2014)

1400064.

- [30] J. Liu, L. Zhang, H.B. Wu, J. Lin, Z. Shen, X.W. Lou, *Energy Environ. Sci.* 7 (2014) 3709-3719.
- [31] Z. Sun, S. Firdoz, E.Y. Yap, L. Li, X. Lu, *Nanoscale*. 5 (2013) 4379-4387.
- [32] J.W. Lee, A.S. Hall, J.-D. Kim, T.E. Mallouk, *Chem. Mater.* 24 (2012) 1158-1164.
- [33] X. Lu, D. Zheng, T. Zhai, Z. Liu, Y. Huang, S. Xie, Y. Tong, *Energy Environ. Sci.* 4 (2011) 2915-2921.
- [34] L. Bao, J. Zang, X. Li, *Nano Lett.* 11 (2011) 1215-1220.
- [35] J. Xiao, L. Wan, S. Yang, F. Xiao, S. Wang, *Nano Lett.* 14 (2014) 831-838.
- [36] Y. He, G. Li, Z. Wang, C.Y. Su, Y. Tong, *Energy Environ. Sci.* 4 (2011) 1288.
- [37] P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhou, C.P. Wong, Z.L. Wang, *ACS Nano*. 7 (2013) 2617-2626.
- [38] X. Yang, C. Cheng, Y. Wang, L. Qiu, D. Li, *Science*. 341 (2013) 534-537.
- [39] Z. Song, L. Chen, J. Hu, R. Richards, *Nanotechnology*. 20 (2009) 275707.
- [40] P. Jeevanandam, Y. Koltypin, A. Gedanken, *Nano Lett.* 1 (2001) 263-266.
- [41] M.B.J.G. Freitas, *J. Power. Sources*. 93 (2001) 163-173.
- [42] M. Toupin, T. Brousse, D. Bélanger, *Chem. Mater.* 14 (2002) 3946-3952.
- [43] F. Xiao, Y.L. Xu, *Int J. Electrochem Sc.* 7 (2012) 7440-7450.
- [44] C. Julien, M. Massot, S. Rangan, M. Lemal, D. Guyomard, *J. Raman. Spectrosc.* 33 (2002) 223-228.
- [45] L. Mao, K. Zhang, H.S. On Chan, J. Wu, *J. Mater. Chem.* 22 (2012) 1845-1851.
- [46] M. Winter, R.J. Brodd, *Chem. Rev.* 104 (2004) 4245-4270.

- [47] S. Kim, J.K. Noh, S. Yu, W. Chang, K.Y. Chung, B.W. Cho, *J. Electrochem. Soc.* 30 (2013) 159-165.
- [48] F. Buciuman, F. Patcas, R. Craciun, D.R.T. Zahn, *Phy. Chem. Chem. Phy.* 1 (1999) 185-190.
- [49] P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845-854.
- [50] C.C. Hu, C.C. Wang, *J. Electrochem. Soc.* 150 (2003) A1079.
- [51] Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao, E. Xie, *ACS Nano.* 7 (2013) 174-182.
- [52] M.G. Hahm, A. Leela Mohana Reddy, D.P. Cole, M. Rivera, J.A. Vento, J. Nam, H.Y. Jung, Y.L. Kim, N.T. Narayanan, D.P. Hashim, C. Galande, Y.J. Jung, M. Bundy, S. Karna, P.M. Ajayan, R. Vajtai, *Nano Lett.* 12 (2012) 5616-5621.
- [53] Y. Zhao, Y. Meng, P. Jiang, *J. Power. Sources.* 259 (2014) 219-226.
- [54] S.W. Lee, J. Kim, S. Chen, P.T. Hammond, Y. Shao-Horn, *ACS Nano.* 4 (2010) 3889-3896.
- [55] J. Liu, J. Jiang, C. Cheng, H. Li, J. Zhang, H. Gong, H.J. Fan, *Adv. Mater.* 23 (2011) 2075-2075.
- [56] Y. Qiu, K. Yan, S. Yang, L. Jin, H. Deng, W. Li, *ACS Nano.* 4 (2010) 6515-6526.
- [57] Y. Qiu, X. Zhang, S. Yang, *Phy. Chem. Chem. Phy.* 13 (2011) 12554-12558.
- [58] X. Lu, Y. Zeng, M. Yu, T. Zhai, C. Liang, S. Xie, M.S. Balogun, Y. Tong, *Adv. Mater.* 26 (2014) 3148-3155.
- [59] W. Zilong, Z. Zhu, J. Qiu, S. Yang, *J. Mater. Chem. C.* 2 (2014) 1331-1336.
- [60] T. Zhai, S. Xie, M. Yu, P. Fang, C. Liang, X. Lu, Y. Tong, *Nano Energy.* 8 (2014)

255-263.

[61] P. Yang, Y. Ding, Z. Lin, Z. Chen, Y. Li, P. Qiang, M. Ebrahimi, W. Mai, C.P. Wong, Z.L. Wang, Nano Lett. 14 (2014) 731-736.

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