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1 Introduction

Continuous research endeavors have been directed towards the design of sustainable and flexible energy conversion/storage devices with promising advantages (e.g., portability, stretchability and lightweight), which show potential applications in sensor networks, stretchable integrated circuits, wearable systems for personal multimedia, computing and medical electronics.¹⁻⁷ The emerging flexible supercapacitors are available with large power density, good operational safety, and long cycling life and hence are highly desirable in the modern electrical energy storage field.8-11 Generally, a free-standing and binderless electrode with favorable mechanical strength and high capacitance is regarded as a vital component for the fabrication of high-performance flexible supercapacitors.^{12,13} From this viewpoint, carbon materials (e.g., carbon nanotubes/ nanofibers and graphene) have shown great potential as electrodes of flexible supercapacitors owing to their superior mechanical and electronic properties, as well as excellent

CoMn-layered double hydroxide nanowalls supported on carbon fibers for high-performance flexible energy storage devices[†]

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CoMn-layered double hydroxide (LDH) nanowalls were supported on flexible carbon fibers (CFs) *via* an *in situ* growth approach; the resulting CoMn-LDH/CF electrode delivers a high specific capacitance (1079 F g⁻¹ at 2.1 A g⁻¹ normalized to the weight of the active LDH material) with excellent rate capability even at high current densities (82.5% capacitance retention at 42.0 A g⁻¹). A combined experimental and theoretical study reveals that the dramatic performance enhancement is mainly attributed to the homogeneous and ordered dispersion of metal units within the LDH framework, which enriches the redox reactions associated with charge storage by both Co and Mn. The hierarchical configuration further improves the exposure of active sites and enables a fast charge transfer to the electrode/ electrolyte interface, with CFs serving as both the current collector and binderless electrode. In addition, a solid-state supercapacitor device with good flexibility was fabricated using the CoMn-LDH/CFs, which achieves a specific energy up to 126.1 W h kg⁻¹ and a specific power of 65.6 kW kg⁻¹. By virtue of rational design of the chemical configuration based on CoMn-LDH nanowalls anchored to CFs, which can be potentially used in wearable and miniaturized devices for energy storage.

electrochemical double layer capacitor (EDLC) performance.¹³⁻¹⁶ However, the less active surface of carbon materials normally limits their capacitance; moreover, current flexible supercapacitors show energy densities far below the value required to provide power assists in commercial applications.¹⁷ Therefore, a major challenge for these EDLCs is to boost the energy density to compete with Li-ion batteries for applications in modern high-performance power sources.

Towards this goal, recent advances in flexible and miniature supercapacitors have been driven by the incorporation of an electrochemically active second phase (mainly including pseudocapacitive conducting polymers and transition metal oxides) in carbon-based matrixes to dramatically enhance the electrode capacitance.^{7,8,18-24} In addition, multimetallic oxides/hydroxides are emerging as a new and promising electrode material for high-performance supercapacitors due to their higher activity compared to the corresponding monometallic component.25-29 Layered double hydroxides (LDHs) are a large class of multimetal clay materials that are constituted by brucite layers of metal cations $(M^{2+} and M^{3+/4+})$ octahedrally surrounded by forming $M^{2+}(OH)_6/M^{3+/4+}(OH)_6$ octahedra.³⁰⁻³⁴ hydroxyls Importantly, due to their tunable composition and high dispersion of cations in host layers, transition metal-based LDHs often give rise to intriguing electrochemical/electronic properties and have received broad interest for biosensors, alkaline secondary batteries and supercapacitors.35-39 Based on

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[†] Electronic supplementary information (ESI) available: Calculations, computational details, EDS spectrum, FTIR spectrum, TEM EDS mapping results, XRD pattern and SEM image of the CoMn-LDH powdered sample, additional electrochemical and DFT results. See DOI: 10.1039/c3ta11452j

the above considerations, the incorporation of promising pseudocapacitive LDHs and carbon fibers (CFs) into a sophisticated architecture would be a desirable resolution for a flexible energy storage system. Firstly, the LDH brucite layer provides a well-organized and stable microenvironment to accommodate different active metal units at atomic scale for effective valence interchange and charge transfer. Secondly, due to the flexible 3D conductive networks, the CF backbone can serve as a favorable scaffold for loading active LDHs and lightweight and bendable supercapacitors. achieving Moreover, the hierarchical structure favors the sufficient exposure of the electroactive species, and simultaneously facilitates the ion/electron transport associated with Faradaic redox reactions.

Herein, we report the fabrication of CoMn-LDH nanowalls supported on CFs by a facile *in situ* growth route (shown in Fig. 1a), and demonstrate the great potential of the resulting material as an efficient electrode for supercapacitors. Based on the unique features of LDH and the hierarchical configuration, the CoMn-LDH/CF electrode yields a largely improved pseudocapacitive performance. Density functional theory (DFT) calculations further reveal that the well-organized electronic framework established in the LDH layer guarantees the integration of Co and Mn active sites, accounting for the resulting high capacitance. Moreover, we have successfully fabricated a simple solid-state supercapacitor based on the CoMn-LDH/CF electrode using a polyvinyl alcohol (PVA)/LiOH electrolyte. This device combines flexibility, conductivity, and



Fig. 1 (a) Schematic illustration of the fabrication of CoMn-LDH/CF nanostructure. (b) SEM and optical (inset) images of the pristine CFs. (c) SEM image of the CoMn-LDH/CFs (inset: the enlarged image). (d) EDS mapping results from a single CoMn-LDH/CF. (e) XRD patterns of the CFs (curve a), the CoMn-LDH powdered sample (curve b) and the CoMn-LDH/CFs (curve c).

electrochemical activity and demonstrates excellent energy density and power density, outperforming many other currently available supercapacitors. The present structural and compositional design offers an effective and convenient approach to improve the overall performance of supercapacitors, highlighting the path for its potential in energy management.

2 Experimental details

2.1 Preparation procedures for CoMn-LDH grown on the CFs

The sample of CoMn-LDH/CFs was prepared using a simple in situ growth approach. The synthesis was performed in a beaker under ambient atmosphere. Briefly, an aqueous solution containing $Co(NO_3)_2 \cdot 6H_2O$ (0.003 M), $Mn(NO_3)_2 \cdot 4H_2O$ (0.0015 M) and NH₄F (0.02 M) was prepared in 250 mL of decarbonated water and delivered into a beaker at room temperature and stirred thoroughly for 15 min. The CF substrate was pretreated with concentrated HNO₃ solution and then cleaned in turn in an ultrasonic bath containing deionized water, acetone, ethanol and deionized water for 10 min each. Subsequently, the CF substrate was immersed in the above solution for another 20 min with gentle stirring. A second aqueous solution (60 mL) containing NaOH (0.04 M) and Na2CO3 (0.015 M) was added dropwise over 5 h into the metallic salt solution with vigorous stirring. Air was bubbled throughout the entire addition period for the oxidation of Mn²⁺. The resulting suspension was aged at room temperature for 24 h, and the CFs coated with LDH nanowalls (CoMn-LDH/CFs) were then withdrawn from the solution, washed extensively with water and dried at room temperature. The content of CoMn-LDH material was accurately calculated from the weight difference of the substrate before and after the growth of CoMn-LDH coating ($\sim 0.5 \text{ mg cm}^{-2}$). The areal mass loading can be further enhanced by employing thicker CF substrates.

As comparison samples, CoAl-LDH/CFs and Co(OH)₂/CFs were synthesized by a similar hydrothermal route. For the CoAl-LDH/CF sample, Co(NO₃)₂·6H₂O (1 mmol), Al(NO₃)₃·9H₂O (0.5 mmol), NH₄F (5 mmol) and urea (35 mmol) were dissolved in 50 mL of deionized water with n(Co)/n(Al) = 2 : 1. Subsequently, a piece of the CF substrate was immersed in the aqueous solution at 90 °C for 6 h. The substrate coated with CoAl-LDH was then withdrawn from the solution, washed extensively and dried at room temperature. For the Co(OH)₂/CF sample, the synthetic procedure was similar to the above method except that hexamethylenetetramine was used as a hydrolysis agent and no Al(NO₃)₃·9H₂O was added.

The alkaline PVA/LiOH polymer electrolytes were prepared by a solution casting method.^{22,52} 5 g of PVA and 2.1 g of LiOH·H₂O were dissolved in 50 mL of water with vigorous and continuous stirring for about 2–4 h at 85 °C, until they completely dissolved in water and formed a jelly-like solution. The resulting gel was weighed, and then put into a vacuum oven to evaporate the excess water at 60 °C. The annealed PVA/LiOH polymer gel was weighed again to confirm that the amount of water has been evaporated.

2.2 Material characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-6000 diffractometer, using Cu-K α radiation (0.15418 nm) at 40 kV and 30 mA. The morphology was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) images were recorded with a Philips Tecnai 20 and a JEOL JEM-2010 HR-TEM. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 instrument (Thermo Electron) with Al K α radiation. Raman measurements were carried out with 633 nm excitation by using a confocal Raman microspectrometer (Renishaw, inVia-Reflex, 633 nm). The Fourier-transform infrared (FT-IR) spectra were recorded using a Vector 22 (Bruker) spectrophotometer in the range 4000–400 cm⁻¹ with 4 cm⁻¹ of resolution.

2.3 Electrochemical measurements

A CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Co., China) was utilized for all electrochemical measurements. It should be noted that the resulting CoMn-LDH/CF electrode was made without using any binding materials, which avoids the influence of impurities. For the threeelectrode configuration, the CoMn-LDH/CF acts directly as the working electrode with a saturated Hg/HgO electrode as the reference electrode and a platinum plate as the counter electrode in 1.0 M LiOH. As shown in Fig. 7a, the supercapacitor in a symmetric-cell configuration was assembled using a pair of CoMn-LDH/CF electrodes $(4 \times 0.5 \text{ cm}^2)$ wrapped with the PVA/LiOH polymer electrolyte or separated by the aqueous electrolyte separator (a Whatman glass microfiber filter). The flexible supercapacitor (the weight of the whole device is less than 15 mg with a cylindrical working volume of 7 \times π \times 0.3^2 cm³) was then sealed in a plastic package, in order to prevent potential leakage of the electrolyte. Cyclic voltammogram (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were performed to evaluate the electrochemical performance of symmetric supercapacitors. The CVs were tested in a voltage window between 0 and 1.7 V at a wide range of scan rates, ranging from 20 to 400 mV s⁻¹. The chargedischarge curves were measured in the same voltage window from 1 to 20 A g^{-1} . The EIS was performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 to 100 kHz at open circuit voltage.

3 Results and discussion

3.1 Structural and morphological study of the CoMn-LDH/ CFs

Conductive CFs were used as both the current collector and the electrode (mechanical support) for *in situ* growth of CoMn-LDH nanowalls serving as the active material for pseudocapacitors (Fig. 1b). Individual carbon fibers are well-arranged and the appropriate channels enable effective electrolyte access for mass transportation.⁴⁰ Through a simple *in situ* growth approach, a uniform coating of LDH nanowalls with high

density was formed on the skeleton of CFs (Fig. 1c), giving rise to a simplified, flexible and lightweight architecture. The nanowalls are evenly distributed across the entire surface of each fiber and intersect with each other, with an open and porous structure of relief features (Fig. 1c, inset). The 3D network structure of the CF backbone is retained since the CoMn-LDH coating is relatively thin, as revealed in Fig. 1c. Energy dispersive X-ray spectrometry (EDS) mapping analysis of a single fiber (Fig. 1d) unambiguously confirms a uniform distribution of Co and Mn elements throughout the hierarchical structure. The mapping result is consistent with the EDS spectrum shown in Fig. S1,† in which the Co/Mn molar ratio was found to be 2.15, in line with the nominal ratio (Co: Mn =2:1). The XRD pattern of the CoMn-LDH/CFs (Fig. 1e, curve c) can be indexed to a rhombohedral LDH phase with the refined lattice parameters of a = 3.12 Å and c = 22.84 Å, in accordance with the CoMn-LDH powdered sample used for comparison (Fig. 1e, curve b; its SEM image is shown in Fig. S2[†]). No other crystalline phase was detected, indicating the high purity of the LDH phase grown onto the CFs. The Fourier transform infrared (FTIR) spectrum of the CoMn-LDH/CF sample (Fig. S3[†]) provides evidence for the presence of CO_3^{2-} existing in the LDH gallery (bands at 1063 and 1365 cm⁻¹). Bands observed in the range 500-800 cm⁻¹ are mainly due to M-O, M-O-M, and O-M-O lattice vibrations.

The typical TEM image of the CoMn-LDH nanowalls (Fig. 2a) displays sheet-like morphology with a lateral size of \sim 80 nm, and the thickness of one single LDH platelet is estimated to be \sim 5.1 nm. Clear lattice fringes of 1.56 Å corresponding to the (110) crystal plane of the CoMn-LDH phase were observed in the high-resolution TEM (HRTEM) image (Fig. 2b). Moreover, the fast Fourier transformation (FFT) pattern (Fig. 2b, inset) exhibits hexagonally arranged spots, indicative of the single-crystal structure of the LDH platelet. The chemical compositions of as-prepared CoMn-LDH on CFs were analyzed by X-ray



Fig. 2 (a) TEM image of CoMn-LDH platelets grown on the CFs. (b) HRTEM image of an individual CoMn-LDH nanocrystal (inset: the corresponding FFT pattern). XPS spectra for (c) Co 2p and (d) Mn 2p of CoMn-LDH/CFs.

photoelectron spectroscopy (XPS), as shown in Fig. 2c and d. The Co 2p core lines split into Co $2p_{3/2}$ (780.6 eV) and Co $2p_{1/2}$ (796.7 eV) peaks accompanied by two satellite bands at 785.5 and 802.1 eV (Fig. 2c), indicative of a high-spin Co²⁺ state in the LDH material.⁴¹ The peaks of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ are located at 642.1 and 653.9 eV (Fig. 2d), respectively, with a spin energy separation of 11.8 eV. This result agrees well with that for MnO₂,⁴² indicating that the predominant Mn species within the LDH is Mn⁴⁺.

3.2 Electrochemical properties of the CoMn-LDH/CFs

Electrochemical measurements in a three-electrode configuration were carried out to evaluate the electrochemical performance. Representative cyclic voltammograms (CVs) of the CoMn-LDH/CFs (the Co/Mn ratio of 2; the mass loading of 0.5 mg cm^{-2}) in 1.0 M LiOH aqueous electrolyte at various scan rates are shown in Fig. 3a. The peak current increases with insignificant change in the CV shape as the scan rate increases from 5 to 40 mV s^{-1} , which reveals its good electrochemical reversibility and high power characteristics. Two pairs of redox peaks at ~ 0.15 and 0.58 V during the anodic and cathodic sweeps are clearly observed, indicating a typical pseudocapacitive behavior related to the reversible conversion between the cobalt species (Co²⁺/Co³⁺ and Co³⁺/Co⁴⁺).^{43,44} The presence of Mn(OH)₆ units can lead to extra reversible redox processes by virtue of Li⁺ and OH⁻ from the electrolyte.^{45,46} The oxidation and reduction peaks are gradually enhanced with the increase of Mn content in the LDH host layers (Fig. S4[†]). The highest redox current was observed for the CoMn-LDH/CF sample with a Co/Mn molar ratio of 2, suggesting the feasibility of rationally tuning the transition-metal composition for optimum electrochemical performance. Galvanostatic charge-discharge curves of the CoMn-LDH/CFs were further measured at various current densities (Fig. 3b). The observed mirror-like potential-time response implies the high charge-discharge coulombic



Fig. 3 (a) CVs of CoMn-LDH/CFs at different scan rates. (b) Galvanostatic charge–discharge curves of CoMn-LDH/CFs at various current densities. (c) The specific capacitance of CoMn-LDH/CFs as a function of current density. (d) Cycling performance of the CoMn-LDH/CFs (the inset shows the charge–discharge curves of the last 20 cycles).

efficiency (not less than 99.3%) of the CoMn-LDH/CF electrode at all the current densities. A symmetric triangular shape with well-defined plateaus during the charge-discharge processes is observed, suggesting its good supercapacitive behavior. The specific capacitances of the flexible electrode can be calculated based on the charge-discharge curves, and the typical data are plotted in Fig. 3c. Evidently, the CoMn-LDH/CF electrode demonstrates ultrahigh specific capacitance values of 1079, 992, 959, 941, 920 and 891 F g⁻¹ at 2.1, 4.2, 8.4, 16.8, 25.2 and 42.0 A g^{-1} , respectively (based on the mass of CoMn-LDH). The results reveal that 82.5% of the capacitance is still retained as the charge-discharge rate changes from 2.1 to 42.0 A g^{-1} , demonstrating that it is superior to most previous Co-based or Mn-based conducting matrix composite electrodes.18,44,45,47,48 When the mass loading of LDH was increased to 0.9 and 1.6 mg cm^{-2} , the specific capacitance was reduced, respectively, to 1020 and 997 F g^{-1} at 2.1 A g^{-1} , still retaining relatively high rate capability (Fig. S5[†]). Taking into account the whole mass of the flexible electrode (4.0 mg), a capacitance of 270 F g^{-1} at a current density of 0.5 A g^{-1} can be obtained. Since the contribution from the CFs to the capacitance is negligible (Fig. S6[†]), the main contribution of the measured capacitance of the CoMn-LDH/CFs originates from the redox pseudocapacitance of the LDH species.

A cycling life test over 6000 cycles for the CoMn-LDH/CFs was carried out at 16.8 A g⁻¹ as shown in Fig. 3d. The CoMn-LDH/CF exhibits a good long-term electrochemical stability, which can be verified from the very stable charge-discharge curves for the last 20 cycles (inset: with ~98.7% coulombic efficiency). After long-term cycling, the structural integrity and hierarchical morphology of the electrode are overall preserved without obvious deterioration (Fig. S7[†]). To illustrate the merits of the hierarchical structure, we have also compared the electrochemical behavior of CoMn-LDH/CFs with that of the CoMn-LDH powdered sample (Fig. S8[†]). Both the enhanced currents and depressed peak separation clearly demonstrate the improved kinetics of ion/electron transport as well as the efficient utilization of the electroactive LDH phase in the CoMn-LDH/CF electrode. In such a unique 3D network, the CoMn-LDH nanowalls are anchored to the CF skeleton with good mechanical adhesion, which eliminates the agglomeration of electroactive sites (Fig. S2[†]) and builds up an interpenetrating pathway for fast electrolyte/electron transport. The above results demonstrate the excellent supercapacitive capability of this CoMn-LDH/CF electrode, which meets the requirements of high-performance energy storage devices.

In order to further evaluate the electrochemical benefits of combining Co and Mn species into the LDH matrix, the capacitive properties of $Co(OH)_2/CFs$ and CoAl-LDH/CFs were also studied for comparison. The brucite-like $Co(OH)_2$ consists of a hexagonal packing of hydroxyl ions with Co^{2+} occupying alternate rows of octahedral sites,⁴⁹ which is isostructural with the LDH host layer (Fig. 4a). The two distinct pairs of redox peaks observed in the CV of $Co(OH)_2/CFs$ agree well with previous reports (Fig. 4b, red curves).⁴⁴ In the case of CoAl-LDH/CFs, the CV shows four similar redox peaks with an increased integral area (Fig. 4b, green curves). This phenomenon



Fig. 4 (a) Octahedral unit arrangement in the hydroxide layer for $Co(OH)_2$, CoAl-LDH and CoMn-LDH viewed along the [001] direction. (b) CVs and (c) chargedischarge curves of the $Co(OH)_2$ /CFs, CoAl-LDH/CFs and CoMn-LDH/CFs at the same scan rate and current density.

indicates that the partial isomorphous substitution of Co²⁺ with Al^{3+} in the Co(OH)₂ lattice to form a hydrotalcite-like structure leads to a high dispersion of the Co(OH)₆ unit, thus improving the utilization of Co species in the redox reaction. On further replacing the inactive Al ion by the pseudocapacitive Mn ion, the great contribution of the Mn(OH)₆ unit to the total capacitance can be confirmed, as expected (Fig. 4b, blue curve). In addition to the redox peaks from the Co species, the CV of CoMn-LDH/CFs expands significantly and becomes approximately rectangular with much boosted currents, revealing the effective combination of the active constituents. The CoMn-LDH/CF also demonstrates remarkable changes in galvanostatic charge-discharge behavior, as presented in Fig. 4c. The lower charge plateau and the higher discharge plateau for CoMn-LDH/CFs relative to both the comparison electrodes indicate its enhanced electrochemical reactivity and lower polarization. These comparative results fully illustrate two merits of CoMn-LDH in the application of pseudocapacitor materials. Firstly, the LDH template provides a confined and stable microenvironment, in which different M(OH)₆ units are separated from each other into a highly dispersive arrangement (TEM mapping results of CoMn-LDH are shown in Fig. 5). This feature ensures that both the Co and Mn species participated efficiently in the Faradic reaction and simultaneously avoids the undesired contact resistance between different phases arising from hybridization of various metal oxides. Secondly, the homogeneity of the local octahedral environments in the LDH layer (Fig. 4a) allows the structural coordination and pseudocapacitive integration of metal cations, boosting the chargetransfer-reaction capacitance. As a result, the clean and welldispersive multi-metal units at the atomic scale using the unique LDH template achieve a highly enhanced pseudocapacitive behavior. More notably, our electrode design protocol can be readily extended to other active transition metals. For



Fig. 5 TEM EDS mapping results from a single CoMn-LDH platelet, showing a uniform and homogeneous distribution of both Co and Mn in the LDH layer.

example, Fig. S9[†] presents the SEM and EDS observations of NiMn-LDH/CFs through the same procedures, which is promising in energy- and environment-related applications.

3.3 Theoretical calculations

To gain further insight into the intrinsic activity of the present multimetallic homostructure (LDH), density functional theory (DFT) calculations were conducted to elucidate the electronic structure of the CoMn-LDH from a theoretical viewpoint. An ideal LDH host layer containing 6 Co atoms and 3 Mn atoms was built on the basis of each $Mn(OH)_6$ octahedron surrounded by six Co(OH)₆ octahedra; three carbonate anions were added into the interlayer region to keep the system neutral (the optimized structure is shown in Fig. 6a). Electron density plots are



Fig. 6 (a) The optimized supercell model for the CoMn-LDH with a 3 \times 3 \times 1 rhombohedral lattice viewed along the [001] direction; (b) electron density contour map of the CoMn-LDH layer viewed along the [001] direction; (c) the total and partial density of states for the CoMn-LDH system (dashed line stands for Fermi level).

created by applying the density contours on the plane with metal-O bonds (Fig. 6b). The Co-O and Mn-O bonds present a mixture of covalent and ionic bonding characteristics due to their partial superimposition of electron densities. Recent research studies have shown that the extra charge compensation at oxygen sites appears to be favored for redox reactions in metal oxides, especially mixed-valent oxides.^{50,51} In this respect, the O atoms with efficient charge accumulation can serve as individual centers to electronically communicate with the adjacent Co or Mn species, resulting in a well-organized and homogeneous framework for facile charge hopping in the LDH layer. Fig. 6c shows the densities of states (DOS) as well as the partial densities of states (PDOS) for the CoMn-LDH model, from which it was found that the highest occupied molecular orbital (HOMO) is mainly composed of O 2p orbitals and the lowest unoccupied molecular orbital (LUMO) is mainly dominated by Co and Mn 3d orbitals (the DOS and PDOS for the CoAl-LDH and $Co(OH)_2$ are shown in Fig. S10[†]). Additionally, Co and Mn 3d orbitals also make contributions to the HOMO, confirming the covalent interaction in both Co-O and Mn-O bonding. It is noteworthy that the Fermi level locates at the p states from O and d states from Co and Mn, demonstrating good hybridization of the O 2p and Co and Mn 3d orbitals. This observation is in line with the high electron delocalization and electrochemical integration of the Co(OH)₆ and Mn(OH)₆ units.

3.4 Supercapacitor assembly and testing

Although significant progress on supercapacitors has been made in hybrid electric vehicles and backup energy sources, a huge challenge remains to achieve high efficiency miniaturized energy storage devices that are compatible with flexible/wearable electronics.^{10,21} In this work, we explored the fabrication of a simple solid-state supercapacitor device, by wrapping two identical CoMn-LDH/CF electrodes with the PVA/LiOH polymer electrolyte (Fig. 7a and S11[†]). This assembly configuration ensures that every single CoMn-LDH/CF composite is efficiently accessible to the electrolyte and utilized for charge storage. The as-fabricated supercapacitor is lightweight (the whole mass is less than 15 mg with a cylindrical working volume of 7 \times π \times 0.3² cm³) and highly flexible, and can be bent without destroying its structural integrity. In order to verify the flexibility of this device, its electrochemical properties were tested under bending conditions. The change in the CV curves collected with different bending angles is insignificant (Fig. 7b). After being bent to 120° 100 times, the device still shows good cycling stability: <4% decrease after 1000 cycles (Fig. S12†). The cycling performance of the flexible device with a bending angle of 120° was also tested; the resulting capacitance retained 93% of its initial value, indicating its excellent mechanical and flexible properties (inset of Fig. S12[†]). The CVs of this device obtained in a wide potential range from 0 to 1.7 V (Fig. 7c) show the absence of redox peaks, indicating that the electrodes undergo a pseudoconstant charge-discharge rate process over the entire voltammetric cycle.40 Furthermore, the device still maintains a relatively rectangular-shaped CV even at a high potential scan rate of 400 mV s⁻¹. The galvanostatic charge-discharge curves



Fig. 7 (a) A schematic representation of the assembled structure and optical photographs (inset) under bending conditions of the supercapacitor device. (b) CVs collected at a scan rate of 400 mV s⁻¹ under different bending conditions. (c) CVs of the device at various scan rates. (d) Galvanostatic charge–discharge curves of the device at various current densities. (e) Electrochemical impedance spectrum of the device. (f) Galvanostatic charge–discharge curves for the one-supercapacitor device and the two-supercapacitor tandem device (inset: LED lighting demonstration, powered by the two-supercapacitor tandem device).

of this device ranging from 1.0 to 20.0 A g⁻¹ are presented in Fig. 7d. The linear symmetric charging–discharging profiles indicate a good capacitive behavior with a rapid *I–V* response. The intercept of the Nyquist curve on the real axis is about \sim 1.1 Ω , as determined in Fig. 7e, manifesting the good conductivity of the electrolyte and low internal resistance for the whole device.

The corresponding energy and power density were obtained from charge-discharge curves at different current densities, based on the mass of CoMn-LDH material. The estimated specific energy density reaches 126.1 W h kg⁻¹ at a power density of 1.7 kW kg⁻¹ and shows little dependence on the cycling rate, still retaining 109.8 W h kg $^{-1}$ at a power density up to 35.9 kW kg⁻¹ (Fig. S13[†]). These values are superior to the previously reported metal oxide/carbon systems.52-57 Additionally, the value of maximum specific power is up to 65.6 kW kg^{-1} , which is much higher than that of other pseudocapacitors.^{23,43,58,59} To evaluate the feasibility of the solid-state electrolyte, the electrochemical stability of the device was examined at a current density of 2 A g⁻¹. The device using PVA/LiOH electrolyte shows greatly improved stability with high capacitance retention of 88.3% after 6000 cycles (Fig. S14a†), which is comparable to the same CoMn-LDH/CF electrode tested in 1 M LiOH aqueous electrolyte. Significantly, the rate capability of the solid-state device is also close to that measured in 1 M LiOH

at the same current density (Fig. S14b†), indicating the efficient mass diffusion in the polymer electrolyte. The results prove that the present solid-state supercapacitor stabilized by the polymer electrolyte maintains excellent electrochemical performances. To demonstrate the practical application of the solid-state device, we fabricated two single supercapacitors in series. This tandem device exhibits an enhanced potential window up to 3.2 V, which can power a light-emitting diode (LED) for $\sim 20 \text{ min}$ after charging at 2.0 A g⁻¹ for 150 s (Fig. 7f).

4 Conclusions

In summary, a facile, cost-effective scalable one-step synthetic route has been developed to produce well-designed CoMn-LDH nanowalls on the surface of flexible CFs for supercapacitor applications. This tailored architecture and the intrinsic features of LDH (environmental homogeneity and electronic pathways) endow the electrode with excellent capacitive performance, e.g., a high specific capacitance, good rate capability and cycling stability, high power capability and energy density, making it a promising candidate material for highperformance energy storage devices. Furthermore, the facile and low-cost assembly of the solid-state supercapacitor leads to a simplified, highly flexible, and lightweight architecture, while exhibiting excellent energy density and power density. By virtue of the simple scale-up method and the synergistic effect of individual constituents, the present strategy can be readily generalized to other electroactive metal hydroxides, such as Ni, Fe, Cu, and Ti, to build multifunctional materials for a large spectrum of energy systems.

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