

Communication

Carbon modified transition metal oxides/hydroxides nanoarrays toward high-performance flexible all-solid-state supercapacitors



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ABSTRACT

Flexible solid-state supercapacitors (FSSCs) have attracted increasing interest for the development of portable and wearable electronics. However, the widely application of FSSCs has been limited by relatively deficient of the electrode materials, such as low electrical conductivity and modest reaction kinetics, which limit the practical energy output and stability. Herein, we introduce the design and fabrication of a sophisticated FSSCs device which consists of conducting carbon materials modified transition metal oxides/hydroxides nanorod arrays (NRAs). The well-defined carbon conducting layer was rationally introduced on the micro NRAs substrate by using metal-organic framework (MOF) as precursor, which was epitaxial grown on the surface of ZnO NRAs. Subsequently, the as-synthesized ZnO@MOF core-shell NRAs were transformed to the well-uniformed ZnO@C@CoNi-layered double hydroxide (LDH) and Fe₂O₃@C core-shell NRAs through *in situ* electrodeposition and cation exchange strategy, respectively. Furthermore, an asymmetric ZnO@C@CoNi-LDH//Fe₂O₃@C FSSC device was constructed with a high energy density (1.078 mW h cm⁻³), power density (0.4 W cm⁻³) as well as outstanding cycling lifespans (retention 95.01% after 10,000 charge/discharge cycles), which is superior to majority asymmetric FSSCs.

1. Introduction

Recently, portable/wearable flexible electronics have attracted considerable attention with the advantages of foldability, light weight as well as facile manipulation. Supercapacitors (SCs), which play a transitional role between conventional capacitors and batteries, have become a type of promising energy storage devices owing to their high power density, moderate energy density and long cycle stability [1–4]. Especially, the flexible solid-state SCs (FSSCs) demonstrate large potential in the development of wearable energy devices by virtue of their remarkable mechanical properties [5–8]. Although the performance of SCs has been greatly improved in the past decades, the practical applications of FSSCs are still hindered by the deficiencies of electrode materials, such as low energy density and narrow electrochemical window. As a result, further efforts are still urgent to tackle these problems of electrode materials for the development of advanced portable/wearable electronics.

Transition metal oxides/hydroxides have shown promising pseudocapacitance property both in aqueous and non-aqueous electrolytes due to their high theoretical capacity [9–15]. However, the intrinsically low electrical conductivity and modest reaction kinetics limit their practical energy output. To overcome these drawbacks, an effective

strategy is to combine pseudocapacitive materials with conducting intermedium for largely enhanced energy density and rate capability [16–23]. Unfortunately, an inevitable phase separation between pseudocapacitive sites and conducting layer, especially after long cycles, severely decreases the SCs performances in both aqueous and solid-state electrolytes. In addition to the problems of electrode materials, a highly-matched SCs configuration is also in demand to guarantee the maximum output of SCs [24]. From the viewpoint of practical applications, the rational design of electrodes with optimized interface of redox materials/conductive additives as well as efficient anode/cathode electrode coupling are both requirements for the transition metal oxides/hydroxides-based SCs devices, which will demonstrate large potential in providing both high energy and power density.

Herein, we present the design and fabrication of a sophisticated FSSCs device which consists of carbon materials connected transition metal oxides/hydroxides nanorod arrays (NRAs). The electron transfer carbon layer is rationally introduced on the surface of metal hydroxides/oxides (layered double hydroxide (LDH) and Fe₂O₃) by using a sacrificial template strategy to make the pseudocapacitance material and conductive carbon material firmly combined together. Moreover, the obtained hierarchical core-shell NRAs guarantee high electrochemical specific surface area to provide abundant active sites.

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Typically, the anode was prepared as follows: a hydrothermal growth of zeolitic imidazolate framework-8 (ZIF-8) coating on the surface of ZnO NRAs was performed, followed by a pyrolysis process to obtain ZnO@C composite material; subsequently, a shell of CoNi-LDH was coated on the exterior surface to attain ZnO@C@CoNi-LDH NRAs. In addition, the cathode was prepared by the transformation of ZnO@ZIF-8 NRAs to Fe₂O₃@C NRAs via a Fe-Zn cation exchange, followed by a further pyrolysis process. As a result, an asymmetric FSSCs device is constructed by employing the well-defined ZnO@C@CoNi-LDH NRAs and Fe₂O₃@C NRAs, which exhibits excellent supercapacitive performances with a high energy density (1.078 mW h cm⁻³), power density (0.4 W cm⁻³) as well as outstanding cycling lifespans (retention 95.01% after 10,000 charge/discharge cycles). It is worth mention that the energy density in this work, is superior to majority asymmetric FSSCs.

2. Experimental section

2.1. Preparation of ZnO@C@CoNi-LDH core-shell NRAs

The ZnO NRAs grown on a nickel foam substrate was prepared by a facile hydrothermal synthesis method [25]. It has been reported that ZnO can be used as self-sacrificial precursor for the *in situ* nucleation and epitaxial growth of ZIF-8 [26,27]. In this work, the Ni foam supported ZnO nanorod arrays (NRAs) were used as self-sacrificial template to provide Zn ions and a skeleton for the growth of ZIF-8. In a typical experiment, 2-methylimidazole (2 mmol) was added into a 16 mL of DMF/H₂O solvent (3:1, v/v), sonicated for 5 min, which was then transferred into a Teflon lined stainless-steel autoclave (25 mL). A piece of nickel foam (2×5 cm²) coated with ZnO NRAs was immersed to the autoclave, sealed and heated at 70 °C for 24 h. The as-obtained product was washed with DMF and absolute ethanol thoroughly, followed by annealing at 650 °C in N₂ gas (2 h) for the preparation of final ZnO@C NRAs. Finally, the nickel foam with ZnO@C NRAs was used as the working electrode with Pt wire as counter electrode and saturated calomel electrode (SCE) as the reference electrode. The electrolyte for the synthesis of CoNi-LDH was obtained by dissolving CoCl₂·6H₂O (1.78 g) and Ni(NO₃)₂·6H₂O (2.18 g) in 50 mL of distilled water. The potentiostatic deposition was carried out at a potential of -1.0 V *versus* SCE. And the weight of ZnO@C@CoNi-LDH is 2.80 mg cm⁻².

2.2. Preparation of Fe₂O₃@C core-shell NRAs

The nickel foam substrate with as-synthesized ZnO@ZIF-8 NRAs was placed into a 50 mL aqueous solution containing 0.27 g of Fe(NO₃)₃·9H₂O and kept at room temperature (2 h) for a Fe-Zn cation exchange reaction. Subsequently, the product was withdrawn, dried in the air and annealed at 450 °C in N₂ for 5 h, to obtain the Fe₂O₃@C core-shell NRAs. And the weight of Fe₂O₃@C NRAs is 2.77 mg cm⁻².

2.3. Preparation of the solid electrolyte

The polyvinyl alcohol (PVA) (molecular weight: 75,000–80,000)–KOH solid electrolyte was prepared as follows: PVA (3.0 g) and KOH (3.0 g) were dissolved in distilled water (30 mL) with vigorous and continuous stirring at 85 °C for 5 h. As a result, a jelly-like solution was formed, which was then placed in air to evaporate excess water.

2.4. Fabrication of ZnO@C@CoNi-LDH//Fe₂O₃@C SC device

The ZnO@C@CoNi-LDH//Fe₂O₃@C FSSC device (area: 1 cm × 1 cm) was fabricated by assembly of a PVA–KOH solid electrolyte membrane, the ZnO@C@CoNi-LDH/nickel foam and the Fe₂O₃@C/nickel foam electrode. The solid electrolyte was installed between the above two electrodes, which was integrated together by mechanical press. The thickness of the all-solid-state EC is ~0.04 cm.

2.5. Characterization

Shimadzu XRD-6000 diffractometer using a Cu Kα source and confocal Raman microspectrometer (Renishaw, inVia-Reflex, 633 nm) were used to measure the X-ray diffraction patterns and Raman spectra of samples, respectively. Thermo VG ESCALAB 250 X-ray photoelectron spectrometer was used for the X-ray photoelectron spectra (XPS) of samples with the pressure of ~2 × 10⁻⁹ Pa and Al Kα X-rays excitation source. Scanning electron microscope (SEM) images, combined with energy dispersive X-ray spectroscopy (EDS), were recorded with Zeiss SUPRA 55 scanning electron microscope (accelerating voltage of 20 kV). Transmission electron microscopy (TEM) images were obtained by Philips Tecnai 20 and JEOL JEM-2010 high-resolution transmission electron microscopes with an accelerating voltage of 200 kV.

2.6. Electrochemical performance measurements

Electrochemical measurements of electrode and device were tested by using a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China). For the electrode tests, a conventional three-electrode cell was used at room temperature in 1 M KOH aqueous solution, combined with Pt wire and SCE as the counter and reference electrode respectively.

The specific capacitance C (F cm⁻²) was determined by means of galvanostatic charge/discharge test based on the following equation:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

where I (mA cm⁻²) is the discharge current normalized to the unit area of the work electrode; Δt (s) is the discharge time, and ΔV (V) means the potential difference.

Energy density and power density of the flexible SC device were calculated using the following equations:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

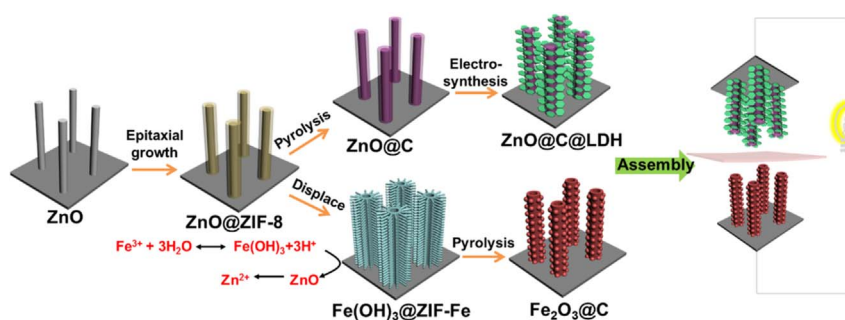
$$E = \frac{C \times \Delta V^2}{2} \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

where C is the capacitance of SC device and I (mA cm⁻²) is the constant discharge current normalized to the unit area of the SC device; ΔV (V) refers to the potential change within the discharge time Δt (s); E (mW h cm⁻³) and P (mW cm⁻³) denote the volumetric energy density and power density, respectively.

3. Results and discussion

The preparation process of the ZnO@C@CoNi-LDH NRAs is illustrated in Scheme 1. Firstly, ZnO NRAs were grown vertically on the surface of a nickel foam substrate via a hydrothermal method. A ZIF-8 layer was coated on the surface of ZnO NRAs though a sacrificial template method, followed by a subsequent transformation to amorphous carbon network via a pyrolysis treatment at 650 °C in N₂ flow. Finally, a shell of CoNi-LDH nanoplatelet arrays were deposited on the exterior surface via an electrosynthesis strategy. SEM image of the ZnO NRAs shows an average diameter of ~60 nm (Fig. 1a). After coated with ZIF-8, the diameter of the ZnO@ZIF-8 nanorod is increased to about 180 nm (Fig. 1b and S1). The ZIF-8 layer was further transfer into highly-porous amorphous carbon networks by a subsequent pyrolysis process. As a result, a uniform carbon layer is formed on the surface of ZnO nanorods to give a three-dimensional (3D) network structure and the diameter of the obtained ZnO@C core-shell NRAs is about 140 nm (Fig. 1c). In addition, elemental contents of Zn, O, C and N of ZnO@C NRAs are determined by EDX spectra to be 15.17%, 44.05%, 35.36%



Scheme 1. Schematic illustration for the fabrication of ZnO@C@CoNi-LDH and Fe₂O₃@C core-shell NRAs for the asymmetrical FSSC.

and 5.43%, respectively (Fig. S2). Finally, CoNi-LDH nanoplatelet arrays were grown on the surface of ZnO@C via electrosynthesis strategy and ZnO@C@CoNi-LDH core-shell NRAs with uniform size and morphology are obtained (Fig. 1d). Fig. S3 shows the SEM images of ZnO@C@CoNi-LDH core-shell NRAs synthesized with various LDH electrodeposition time. The thickness of LDH layer raised along with the increase of preparation time. When the electrodeposition time was 100 s, the layer of LDH was coated on the ZnO@C NRAs completely. This hierarchical nanostructure is further confirmed by TEM image

(Fig. 1e and f). As indicated by the lattice fringes, the *d*-spacing is ≈ 0.25 nm and 0.26 nm for the shell and core, corresponding to the LDH (012) plane and the (002) planes of ZnO. Between the LDH and ZnO, a thin layer of amorphous carbon can be observed, indicating the successfully introduction of the carbon interlayer in this system (Fig. 1f). In addition, the core-shell structure of ZnO@C@CoNi-LDH NRAs was further identified by the EDS mapping analysis (Fig. 4g), in which Zn and O are distributed the core region while the C in the middle layer. Co and Ni are located homogeneously in the whole

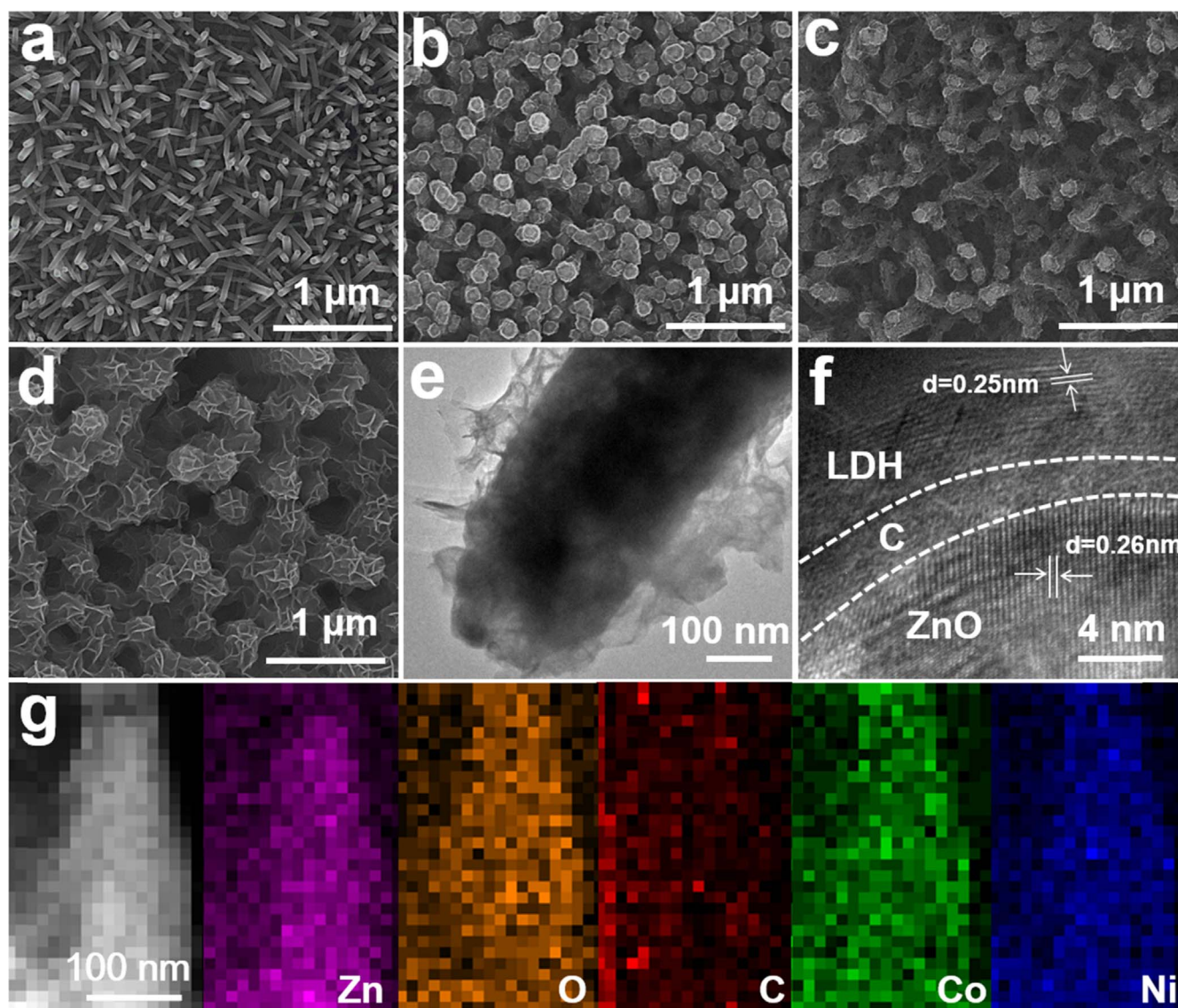


Fig. 1. SEM images of (a) ZnO NRAs, (b) ZnO@ZIF-8, (c) ZnO@C and (d) ZnO@C@CoNi-LDH core-shell NRAs. (e) TEM, (f) HRTEM and (g) EDS mapping of the as-fabricated ZnO@C@CoNi-LDH core-shell NRAs.

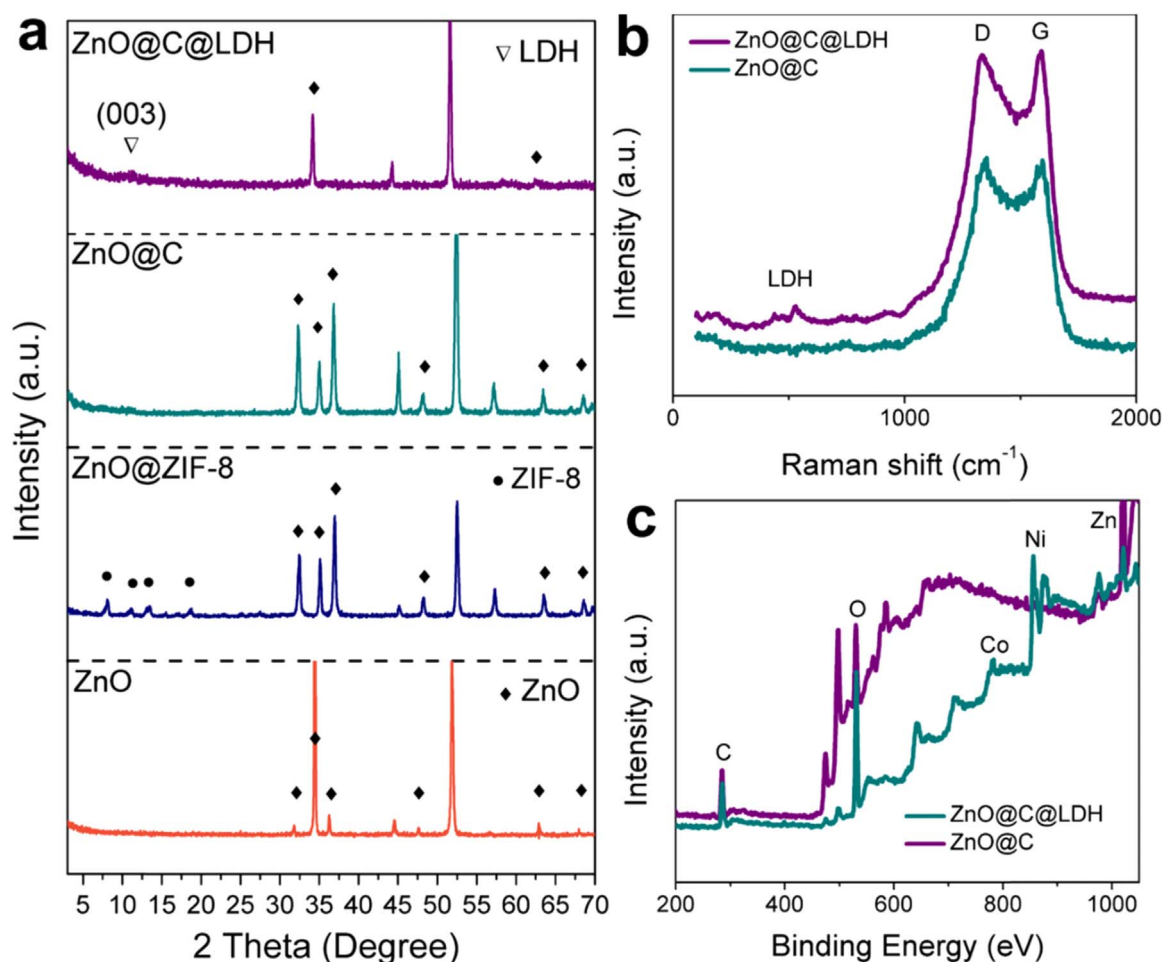


Fig. 2. (a) XRD patterns of ZnO, ZnO@ZIF-8, ZnO@C and ZnO@C@LDH NRAs, respectively. (b) Raman and (c) XPS spectra of ZnO@C and ZnO@C@LDH NRAs, respectively.

nanorod shell.

The chemical structure and composition of the core-shell NRAs were further studied by X-ray diffraction, Raman spectra and XPS technique. Fig. 2a shows the XRD patterns of ZnO, ZnO@ZIF-8, ZnO@C, ZnO@C@LDH NRAs, respectively. ZnO NRAs with dominant (002) reflection confirms their preferential anisotropic growth along the vertical direction of nickel foam. The ZnO@ZIF-8 NRAs sample displays a superimposition of both ZnO and ZIF-8 phase, indicating an *in situ* growth of ZIF-8 structure on the surface of ZnO NRAs. The following pyrolysis treatment results in the carbonization and disappearance of typical characteristic reflections of ZIF-8, which will be proved by the next Raman and XPS spectrum. In the case of the final product ZnO@C@CoNi-LDH NRAs, besides the ZnO phase, a peak at 2θ 11.71° is observed, which is assigned to the (003) reflection of an LDH phase. Raman spectra of both ZnO@C and ZnO@C@CoNi-LDH NRAs display peaks at 1580 and 1360 cm⁻¹, corresponding to the π -conjugated structure and ring stretching mode of carbon, respectively (Fig. 2b) [28]. After coating with LDH shell, a new peak at 523 cm⁻¹ is observed, which is attributed to the stretching of Metal–Oxygen–Metal bonds between the metal ions on the layers and the anions between the layers of CoNi-LDH [29]. We further regulated the calcination temperature to control the graphitization degree of the carbon layer. As shown in Fig. S4a, the surface of the ZnO NRAs was wrapped with large amounts of nanoparticles under a calcination temperature of 500 °C, indicating not fully transformation of ZIF-8 to carbon materials. After rising the calcination temperature to 650 °C, the carbonization can be achieved more successfully with carbon layers coating firmly on the ZnO NRAs (Fig. S4b). As shown in Raman spectra (Fig. S4d), the intensity ratio of G band to D band (I_G/I_D) for ZnO@C NRAs-650 °C (1.0) is larger than that

of ZnO@C NRAs-500 °C (0.98), further indicating a gradually increased graphitization degree. However, when the pyrolysis temperature is further increased to 800 °C, the NRAs was totally destroyed and dropped from the Ni foam substrate due to the volatilization of Zn substrates [30] (Fig. S4c), giving rise to no characteristic Raman spectrum of carbon (Fig. S4d). In addition, surface elemental analysis was carried out by XPS measurements (Fig. 2c). The ZnO@C sample shows the presence of Zn, O and C element; while ZnO@C@CoNi-LDH demonstrates the existence of Co, Ni, O, Zn, and C element. This indicates the successful coating of CoNi-LDH shell on the surface of ZnO@C.

The electrochemical performance was evaluated in a three electrode configuration in KOH aqueous electrolyte (1.0 M) at room temperature, in which a Pt wire and saturated calomel electrode (SCE) were used as the counter and reference electrode. Fig. 3a shows the cyclic voltammograms (CVs) of ZnO, ZnO@C, ZnO@LDH and ZnO@C@LDH NRAs at a scan rate of 25 mV s⁻¹. For ZnO and ZnO@C NRAs, both of their CV area are negligible compared with that of ZnO@LDH and ZnO@C@LDH NRAs, indicating the CoNi-LDH serves as the main capacitor contributor. The electrochemical performance for the ZnO@C treated at different temperature demonstrates that the ZnO@C NRAs-650 °C is obviously superior to that of ZnO@C NRAs treated at 500 °C (Fig. S4e). Thus, the ZnO@C NRAs-650 °C was used as substrate to anchor the LDHs materials. The CVs curves of ZnO@C@LDH core-shell NRAs with various scan rates can be seen in Fig. S5a. The integral area increases as the increasing of scan rate, indicating a promising rate capability. As shown in Fig. S5b, two pairs of redox peaks can be clearly observed from the CV curve at a slow scan rate of 2 mV s⁻¹: the first redox couple (P1 and P2) is due to the Co²⁺/Co³⁺ reaction; while the second redox

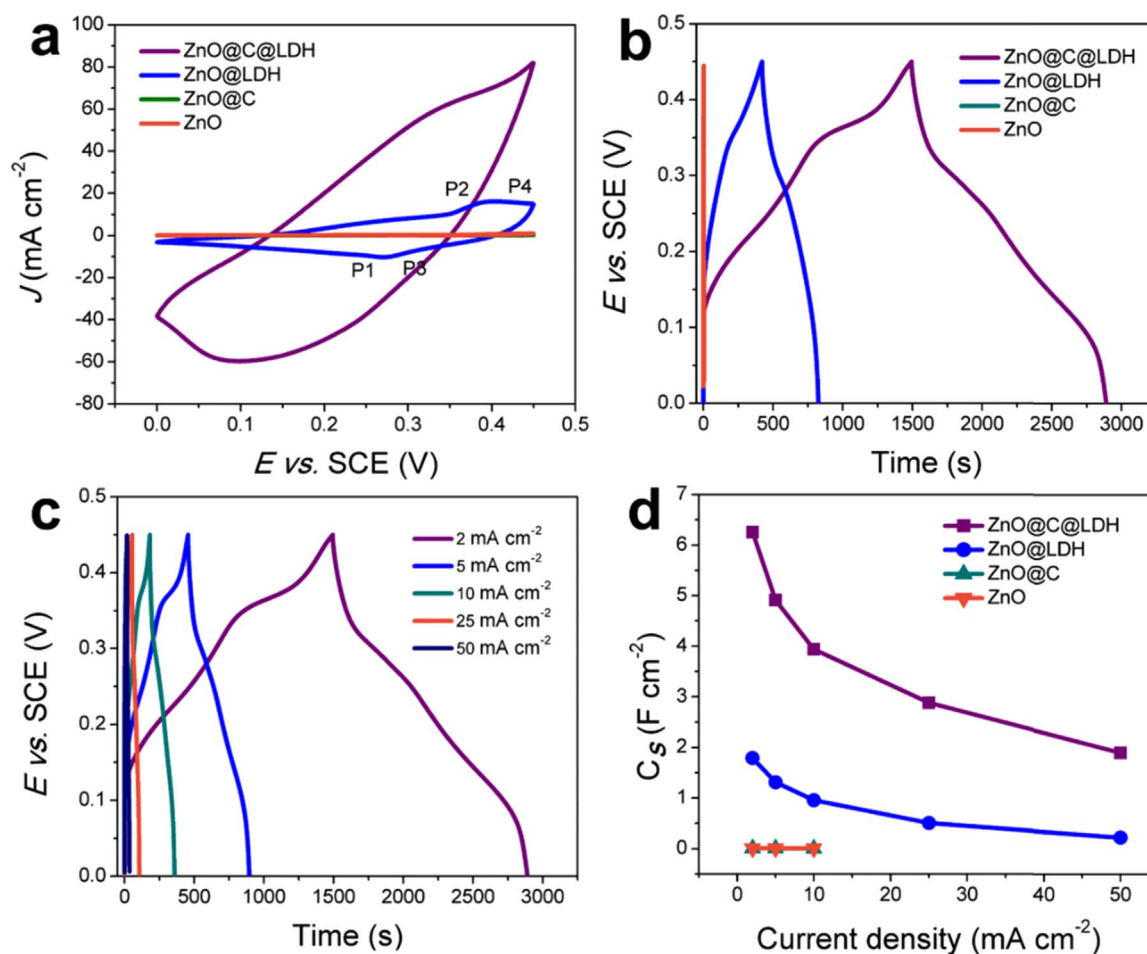


Fig. 3. (a) CV and (b) GV charge/discharge curves for the ZnO, ZnO@C, ZnO@LDH and ZnO@C@LDH NRAs. (c) GV charge/discharge curves for ZnO@C@LDH NRAs at various current densities. (d) Specific capacitance as a function of current density for the ZnO, ZnO@C, ZnO@LDH and ZnO@C@LDH NRAs, respectively.

couple (P3 and P4) are attributed to the $\text{Ni}^{2+}/\text{Ni}^{3+}$ conversion [31,32]. This indicates a pseudocapacitive behavior for the ZnO@CoNi-LDH NRAs, which mainly contributed by CoNi-LDH. Fig. 3b shows the galvanostatic (GV) charge/discharge curves of these four samples (current density: 2 mA cm⁻²; potential range: 0–0.45 V), which exhibit a typical pseudo-capacitive behavior, consistent with the results of CVs. The corresponding specific capacitance are 0.0049, 0.0086, 1.7867, 6.2578 F cm⁻² for ZnO, ZnO@C, ZnO@LDH and ZnO@C@LDH NRAs, respectively, demonstrating the optimal specific capacitance of ZnO@C@LDH sample. This is, to the best of our knowledge, the largest value among LDH-based electrodes ever reported [33–37]. Rate capability is another key factor for evaluating the power application of SCs, which is determined by using the GV technique at different charge/discharge current densities (Fig. 3c). The ZnO@C@LDH NRAs electrode yields a substantially higher specific capacitance than that of the other three samples (Fig. 3d), which can maintain 62.9% at a current density of 10 mA cm⁻² and 30.4% at 50 mA cm⁻². In contrast, the specific capacitance of ZnO@LDH without carbon layer only gives 53.5% and 12.5% cm⁻² at 10 mA cm⁻² and 50 mA cm⁻², respectively.

The results above indicate that the introduction of carbon layer largely facilitates the electrochemical activities of LDHs-based pseudocapacitive materials. The enhanced performance of ZnO@C@LDH NRAs was further confirmed by the electrochemical impedance spectroscopy (EIS) measurements. Fig. S6 shows the Nyquist plots of EIS spectra for substrate (nickel foam), ZnO@LDH, and ZnO@C@LDH NRAs. All these curves consist of a semicircle in high frequency region and a straight line in low frequency region. The ZnO@C@LDH NRAs electrode shows a smaller semicircle diameter and larger slope

compared with other electrodes, which indicates a faster electron transport kinetics and ion diffusion rate at the electrode /electrolyte interface [38,39]. Thus, the highly-porous carbons improve the electronic conductivity of LDH, which facilitates the effective Faradic redox reaction of the electrode materials.

The preparation of $\text{Fe}_2\text{O}_3/\text{C}$ NRAs is shown in Scheme 1. The ZnO@ZIF-8 NRAs was immersed into an aqueous solution containing Fe^{3+} for 2 h at room temperature, leading to the transformation of ZnO@ZIF-8 NRAs to $\text{Fe}(\text{OH})_3/\text{ZIF-Fe}$ NRAs. After pyrolysis process in a H_2 atmosphere at 450 °C, the $\text{Fe}(\text{OH})_3/\text{ZIF-Fe}$ NRAs can be successfully converted to the $\text{Fe}_2\text{O}_3/\text{C}$ NRAs. The as-obtained $\text{Fe}(\text{OH})_3/\text{ZIF-Fe}$ NRAs maintain the rod morphology (with the whole diameter of ~300 nm) coated with plate-like ZIF-Fe on the surface of $\text{Fe}(\text{OH})_3$ (Fig. 4a). After pyrolysis, the outer diameter of $\text{Fe}_2\text{O}_3/\text{C}$ NRAs is distributed within 200–220 nm, as shown in Fig. 4b. Interestingly, Fig. S7a and S7b demonstrates the presence of tubular structure of $\text{Fe}(\text{OH})_3/\text{ZIF-Fe}$ and $\text{Fe}_2\text{O}_3/\text{C}$ respectively. TEM image of $\text{Fe}_2\text{O}_3/\text{C}$ shows that the Fe_2O_3 nanoparticles are coated on the carbon matrix (Fig. 4c). The d-spacing from high resolution TEM (HRTEM) is ~0.25 nm, corresponding to the (110) plane of Fe_2O_3 phase (Fig. 4d). The EDS mapping of $\text{Fe}(\text{OH})_3/\text{ZIF-Fe}$ shows the existence of Fe, O and C but without Zn (Fig. 4e), confirming the complete replacement of Zn by Fe. The resulting $\text{Fe}_2\text{O}_3/\text{C}$ NRAs sample also displays a well-uniformed distribution of Fe, O and C element (Fig. S8). Furthermore, Raman and XPS spectrum of $\text{Fe}_2\text{O}_3/\text{C}$ NRAs (Fig. S9 and Fig. S10) verify the presence of carbon.

Fig. S11a and S11b show the CV curves of $\text{Fe}_2\text{O}_3/\text{C}$ NRAs in 1 M KOH solution at various scan rates (5, 10, 25, 50 mV s⁻¹) and the GV

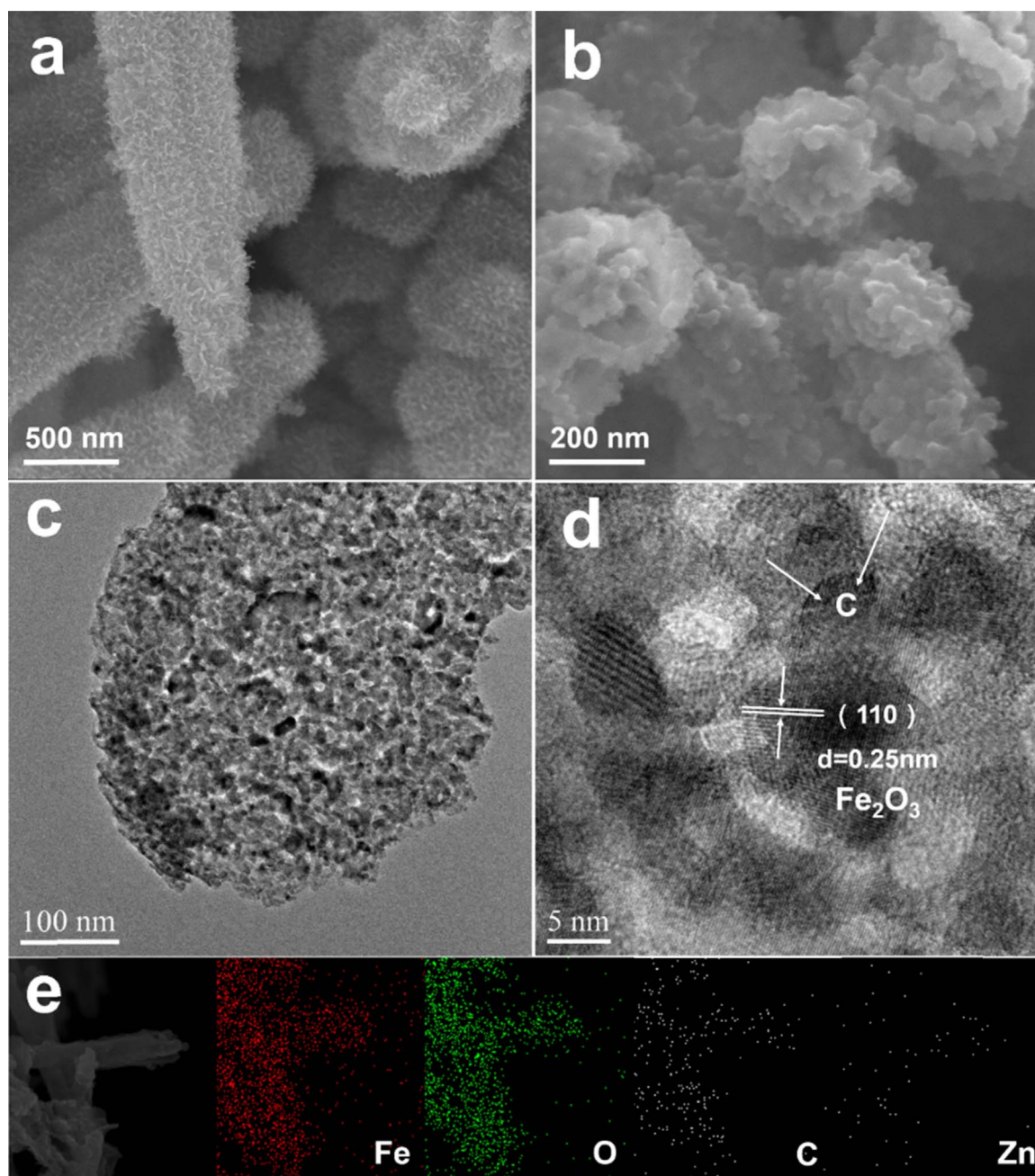
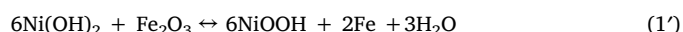


Fig. 4. SEM images of (a) $\text{Fe}(\text{OH})_3$ @ZIF-Fe NRAs and (b) Fe_2O_3 @C NRAs. (c, d) HRTEM images of Fe_2O_3 @C NRAs. (e) EDS mapping for $\text{Fe}(\text{OH})_3$ @ZIF-Fe NRAs.

charge/discharge curves at different current densities (2, 3, 5, 10 mA cm^{-2}) respectively. Two oxidization peaks at -0.91 and -0.65 V are observed in the CV curves, which can be attributed to the formation of $\text{Fe}(\text{OH})_2$ (from Fe^0 to Fe^{2+}) and FeOOH (from Fe^{2+} to Fe^{3+}), respectively. One obvious reduction peak at -0.98 V is assigned to the reduction process of Fe^{3+} to Fe^{2+} . In addition, the capacity of Fe_2O_3 @C NRAs is 0.194 F cm^{-2} at 2 mA cm^{-2} , which is comparable with reported Fe_2O_3 based materials [40,41].

Subsequently, a flexible all-solid-state asymmetric FSSC is further fabricated by using ZnO@C@LDH NRAs as the positive electrode, Fe_2O_3 @C as the negative electrode and poly(vinyl alcohol) (PVA)–KOH as the solid electrolyte. The area of FSSC is 1.0 cm^2 and the thickness is 0.04 cm (Fig. 5a). Fig. 5b shows the CV curves of $\text{ZnO@C@CoNi-LDH//Fe}_2\text{O}_3$ @C device at various scan rates (5 – 100 mV s^{-1}) with the potential window from 0 to 1.6 V , which display a pair of redox peaks due to the following reaction [42]:



The GV charge/discharge results of device with different current densities (1, 2.5, 5, 10, 20 mA cm^{-2}) are shown in Fig. 5c, from which the energy (E) and power (P) density of the FSSC can be obtained (Fig. 5d). The charge/discharge curves of the FSSC device at a current density of 10 mA cm^{-2} remain nearly symmetric at an operating potential as high as 1.6 V (Fig. S12a), suggesting that the device exhibits ideal capacitive characteristics with a rapid I – V response. Fig. S12b displays a variation of the volumetric and specific capacitance of the asymmetric supercapacitor with an increasing potential window. The volumetric capacitance enhances significantly from 3.38 to 30.90 mF cm^{-2} as the operating potential increases from 0.8 to 1.6 V . As a result, the $\text{ZnO@C@CoNi-LDH//Fe}_2\text{O}_3$ @C device gives a maximum energy density of $1.078 \text{ mWh cm}^{-3}$ (at a power density of 0.02 W cm^{-2}) and power density of 0.4 W cm^{-3} (at an energy density of $0.254 \text{ mWh cm}^{-3}$) at an operating voltage of 1.6 V . It is worth mention that the energy

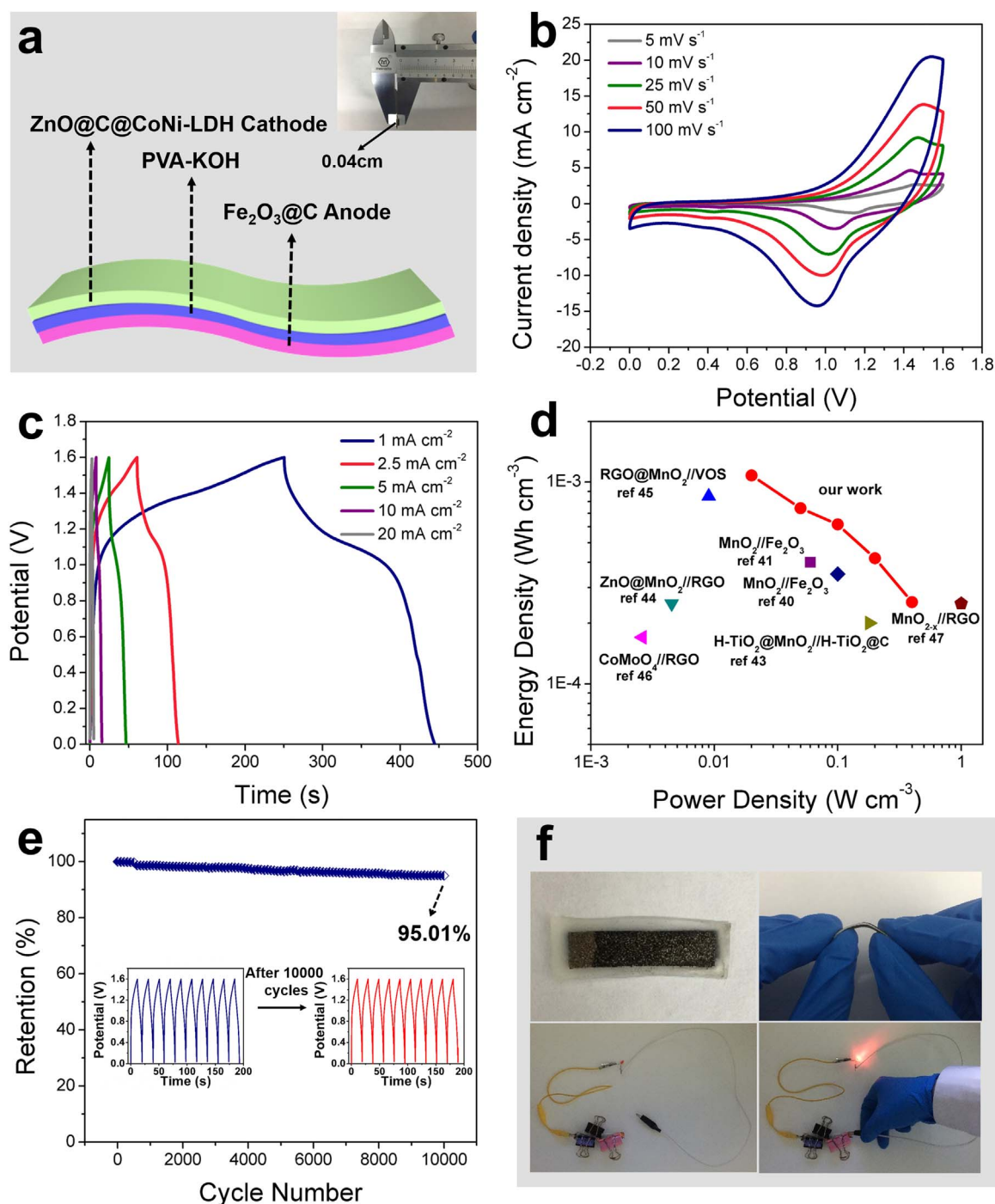


Fig. 5. (a) Schematic representation of the FSSC device based on ZnO@C@LDH, Fe₂O₃@C electrode and PVA-KOH electrolyte. (b) CV and (c) GV curves of the device at various scan rates and current densities. (d) Ragone plots of the FSSC, compared with previous reported results. (e) Cycling performance of the device at a current density of 20 A g⁻¹ (inset: GV results of the first and last 10 cycles). (f) LED lighting demonstration, powered by two FSSC devices in series.

density in this work is superior to the most reported asymmetrical flexible SC devices [40,41,43–47], such as MnO₂//Fe₂O₃ [41], H-TiO₂@MnO₂//H-TiO₂@C [43], ZnO@MnO₂//RGO [44]. Moreover, this FSSC displays excellent long-term cycling stability: a capacitance retention of ~95.01% is obtained after cycling 10,000 times. Highly efficient flexible SCs are attractive for the development of soft and portable electronics. The effect of curvature on this FSSC performance was examined by testing the galvanostatic charge/discharge cycling stability at four different bending angles (from 0° to 180°). As shown in Fig. S13, the specific capacitance maintains 99.71%, 96.36%, 92.93% and 89.07% with a bending angle of 0°, 60°, 120° and 180° respectively,

which can be maintained at nearly a constant value even after each 500 cycles at current density of 2.5 mA cm⁻². Moreover, it is encouraging that the specific capacitance recovered to 98.11% when the bending angle returned to 0°. Fig. 5f displays two FSSC devices in series which power a red LED light bulb (the rated voltage is 2.0–2.2 V), demonstrating its potential application as a flexible SC.

In summary, well-aligned hierarchical carbon connected transition metal oxides/hydroxides NRAs have been successfully fabricated by using epitaxial growth of ZIF-8 as carbon precursor. Benefiting from the specific core-shell heterostructure and the conductivity of carbon layer, both ZnO@C@CoNi-LDH and Fe₂O₃@C NRAs electrodes exhibited

excellent electrochemical performance. Moreover, a flexible all-solid-state ZnO@C/CoNi-LDH/Fe₂O₃@C SC was further constructed, which delivered a surprising high energy density of 1.078 mW h cm⁻³ and excellent cycling stability (95.01% capacitance retention over 10,000 cycles). This work provides a new strategy in the design and preparation of flexible electrochemical energy storage devices based on the cost effectiveness transition metal oxides/hydroxides.

Acknowledgements

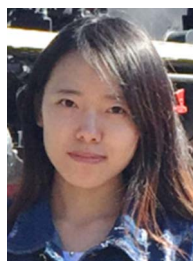
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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2017.09.049>.

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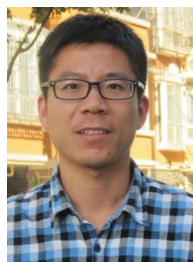
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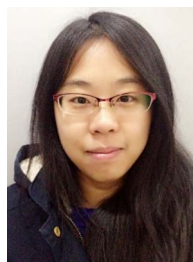
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