Contents lists available at ScienceDirect

## Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

# An ultrafast, high capacity and superior longevity Ni/Zn battery constructed on nickel nanowire array film

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#### ARTICLE INFO

Article history: Received 1 April 2016 Received in revised form 6 July 2016 Accepted 27 July 2016 Available online 28 July 2016

Keywords: Ni/Zn battery Ni nanowire array Ultrafast High capacity Superior longevity

#### ABSTRACT

With the bloom of portable and wearable electronics, electrochemical storage devices featured with high performance, low-cost, safe, environmental-friendly, lightweight, thin and flexible features become more important than ever. Here, we construct a rechargeable Ni/Zn battery with a Co-doped Ni(OH)<sub>2</sub> (CNH) and Zn materials on nickel nanowire arrays (NNA) for electrodes. The CNH cathodic material can be electrochemically deposited onto the NNA, which can deliver a high capacity of 346 mA h g<sup>-1</sup> at current density of 5 A g<sup>-1</sup>. Co doping can effectively stabilize Ni(OH)<sub>2</sub> with only ~10% capacity loss over 5 000 charge/discharge cycles at 30 A g<sup>-1</sup>. For anode, the design of Zn on NNA considerably lowers the risk of corrosion and dendrite form ation. As a result, ultrafast rechargeable Ni/Zn batteries are obtained, exhibiting a cell voltage of ~1.75 V, energy density of 148.54 Wh kg<sup>-1</sup> (4.05 Wh L<sup>-1</sup>) and power density of 1.725 kW kg<sup>-1</sup> (based on the mass of active materials) with a charging time of < 1 min. Additionally, the NNA-based aqueous Ni/Zn battery exhibits superior longevity (only ~12% capacity losses after 5000 cycles). These features enable our Ni/Zn batteries a highly promising candidate for the next generation of flexible energy storage systems.

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#### 1. Introduction

The recent bloom of portable electronics has kindled the strong demand of miniaturized energy storage devices with high energy, long cycling life, and safety characteristics [1–4]. Lithium ion batteries have high energy densities among rechargeable batteries yet they still face the problems e.g. flammability, high cost and insufficiency in power density [5]. On the other hand, traditional aqueous rechargeable batteries are cost effective, safe and can deliver a high power density, yet energy density and cycling capability are limited [6–10]. Among various aqueous rechargeable batteries are a group of rechargeable alkaline batteries based on faradaic reactions, which involve one or multielectron reactions at the electrolyte/electrode interface [7]. Numerous electrochemical redox couples have been explored for alkaline Ni/metal batteries, including Ni/Cd [11], Ni/Zn [12], Ni/Fe

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http://dx.doi.org/10.1016/j.nanoen.2016.07.035 2211-2855/© 2016 Published by Elsevier Ltd. [9], and Ni/Co [7] batteries etc. Among them, Ni/Zn batteries are particularly advantageous, because: i) Zn is highly abundant, environmentally benign, stable in aqueous electrolyte, and has a low equilibrium potential and a high specific capacitance of 820 A h kg<sup>-1</sup> [13]; ii) Ni/Zn batteries are a rechargeable system with high energy and power densities, high working potential, wide working temperature range and abundant of both raw materials [12,13]. However, the cycle life of Ni/Zn batteries is greatly depreciated by the severe capacitance deterioration of Ni(OH)<sub>2</sub> on cathode and the Zn dendrites formation on anode during the repeatedly charge and discharge cycles [11–13]. In order to address the above problems, a few attempts have been made by materials scientists and electrochemists [8-10,12]. For example, Fang and coworkers developed the Ni/Fe alkaline cell based on light weight graphene/carbon nanotubes hybrid films with the energy density of 100.7 Wh kg<sup>-1</sup> [9]; Gong et al. synthesized NiCoAl-layered hydroxide nanoplates attached on carbon nanotubes as the cathode materials for rechargeable Ni/Zn battery [12]. Such attempts can not only bridge the energy density gap between electrochemical capacitor and thin film lithium ion batteries, but also help address the key issues in the next generation flexible energy storage systems.







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Recently, there have been significant advances regarding the miniaturized energy storage technology. Previously, we developed the nickel nanocone array fabrication technology for the construction of ultrathin supercapacitor electrode current collectors [14], which rendered roll-to-roll electrode fabrication technology of supercapacitors. The three dimensional (3D) electrode structure can not only enhance the active mass loading but also facilitate ion and electron transports for an electrochemical energy storage device [15]. Here, we use nickel nanowire arrays (NNA) rooted on a metallic substrate (i.e. Ti foil) as a unique current collector for Ni/ Zn battery electrodes (Fig. 1a). Each nanowire has the length of about 1 mm (Fig. S1), diameter of 130–170 nm, and is vertically oriented to the Ti foil (Fig. 2a and b). The nanowires are metallurgically connected to the substrate film (Fig. S2), which show a spatial packing density of about 2.08 mg cm<sup>-2</sup> [15]. This structure renders the nanostructured current collector flexible, highly conductive and super-hydrophilic, making NNA an ideal framework for supporting nanostructured active materials without adding either polymer binder or conductive additives. In this work, the rechargeable Ni/Zn batteries are constructed by electrodepositing Co-doped Ni(OH)<sub>2</sub> (CNH, cathode material) and Zn (anode material) on the NNA films. Fig. 1 schematically shows the architecture of the two electrodes and the full cell, as well as the working mechanism of the cell. These novel flexible Ni/Zn batteries demonstrate superior energy and power densities stemming from the nano-sized feature of active materials and the hierarchical structure of the hybrid electrodes. Furthermore, long-term (up to 5000) cycling performance for the as-assembled Ni/Zn cells is also achieved in this study.

#### 2. Experimental

#### 2.1. Synthesis of the NNA current collector film

NNA was fabricated by a two-step chemical deposition process. Briefly, a commercial Ti foil (99.99%, thickness ca. 40 µm) was employed as the substrate film. All the solutions in the experiments were prepared with analytical grade chemicals and deionized water. Firstly, a thin layer of Zn was electrodeposited on Ti foil in an aqueous solution containing 1.0 M ZnSO<sub>4</sub> and 3.0 M KCl at a constant current density of  $2 \text{ mA cm}^{-2}$  for 60 s. The Zn deposited Ti film was washed with deionized water and dried in an oven at 60 °C for 2 h, followed by immersing in a plating bath containing 23 mM PdCl<sub>2</sub>, 0.4 vol% HCl, 30 vol% ammonia solution and 5 mM hydrazine at 60 °C for 30 min. After the Pd active layer was deposited, the samples were thoroughly washed with deionized water and dried in air. Then the NNA was in situ deposited onto this film. Briefly, a 50 mL aqueous solution (defined as solution A) containing 0.10 M NiCl<sub>2</sub>, 37.5 mM sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) and 0.20 mM H<sub>2</sub>PtCl<sub>6</sub> was prepared, where another aqueous solution (defined as solution B) containing 8.5 vol% of hydrazine hydrate was added subsequently. Prior to the reaction, the pH value of both the solution A and solution B was adjusted to 12.5 with 6 M KOH aqueous solution at room temperature measured by a pH meter (HORIBA, F-71). Then, a piece of neodymium iron boron magnet was fixed outside a beaker, and the above Ti foil was vertically placed inside the beaker wall opposed to the magnetic field. The foil and magnet were placed as close as possible with each other, so as to allow the magnetic field as strong as possible to pass through the foil. Then solution A and solution B were heated to 80 °C separately followed by mixing them together in that beaker. After 60 min reaction at 80 °C, Ni nanowires eventually grew up to 1 mm long were deposited onto the Pd active layer. Finally, the NNA samples were washed for three times with deionized water and ethanol, and dried in a desiccator at 60 °C for 2 h.

# 2.2. Fabrication of NNA@CNH hybrid cathode and NNA@Zn anode films

CNH nanostructures were electrochemically deposited on NNA film directly in an aqueous solution containing Ni(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>3</sub> (totally 0.1 M), with the mole percentage of Co ranging from 0% to 50%. The electrochemical deposition process was conducted in a three-electrode system at a scan rate of  $100 \text{ mV s}^{-1}$ within the potential window of -1.2-0 V, using saturated calomel electrode (SCE) as reference electrode, Pt foil as counter electrode and NNA film as working electrode. The mass loading of active materials could be adjusted by controlling the CV cycles. Then the NNA@CNH electrode film was washed with deionized water and ethanol, and dried in vacuum, which was ready for use as positive electrode. Zn was deposited on NNA current collector film as negative electrode. The electrodeposition process was conducted at a current density of 2 mA cm<sup>-2</sup> in an aqueous solution containing 1 M Zn(Ac)<sub>2</sub> and 1 M KCl. The NNA was used as working electrode and a piece of Zn foil used as counter electrode. The NNA@Zn electrode film was washed with deionized water and ethanol, and dried in vacuum, which was ready for use as the negative electrode. The mass loading density of Zn and CNH was determined according to the mass change before and after the electrodeposition process.

#### 2.3. Fabrication of aqueous Ni/Zn alkaline battery

A piece of NNA@CNH electrode film and a piece of NNA@Zn electrode film with the same area  $(1 \times 1 \text{ cm}^2)$  were used for assembly. The aqueous full battery was assembled by integrating both anode and cathode films together with a piece of commercial separator (thickness of 100  $\mu$ m, NKK) soaked with aqueous electrolyte solution (1 M KOH) in between the two electrodes.

#### 2.4. Materials characterizations

The morphology and microstructure were characterized by field emission scanning electron microscopy (FE-SEM, HITACH S4800, Japan, working voltage 5 kV) and TEM (FEI-G2 Spirit, Germany, working voltage 300 kV). X-ray photoelectron spectroscopy (XPS) (ESCALASB 250 Xi, Thermo Scientific, USA) measurements were performed to analyze the surface species and their chemical states. The deconvolution and spectral line fitting were carried out using XPS Peak 4.0. The phase and crystallinity analysis was conducted by XRD (BrukerDS RINT2000/PC, Germany) using Cu K<sub> $\alpha$ </sub> radiation with  $\lambda$ =1.5418 Å (at a diffraction angle ranging from 5° to 90° at a scan rate of 5° min<sup>-1</sup>).

#### 2.5. Electrochemical measurement

Cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) and electrochemical impedance spectroscopy (EIS) of the as-prepared samples were investigated on an electrochemical station (VMP3, Bio-Logic, France) by a three-electrode configuration in a KOH (1 M) aqueous electrolyte, where Pt and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The EIS test was conducted in the frequency range between 100 kHz and 0.01 Hz with amplitude of 5 mV at the open-circuit potential.

#### 2.6. Calculations

The specific capacitance ( $C^*$ ,  $F g^{-1}$ ) of CNH samples was calculated from CV with the following equation.



**Fig. 1.** Schematic illustration of the flexible Ni/Zn rechargeable cells. (a) NNA films are used as the current collector for both cathode (Co-doped-Ni(OH)<sub>2</sub>)) and anode (Zn). (b) The Ni/Zn cell structure, working mechanism of the Ni/Zn cell and the involved electrochemical reactions.



**Fig. 2.** Materials characterizations. (a) SEM image of NNA nanostructure. (b) Magnified SEM image of a single piece of nickel nanowire. (c) SEM image of NNA@CNH nanostructure. (d) TEM image of NNA@CNH core-shell nanostructure. (e) Magnified TEM image of NNA@CNH nanostructure (inset: SAED pattern on the hydroxide layer). (f) STEM image focused on a local region of NNA@CNH sample. (g)–(i) EDS-mappping images of the distribution of Ni, Co and O elements.

$$C^* = \frac{\int I(V) dV}{\Delta V \cdot v \cdot m}$$
(1)

where I(V) was the voltammetry current, v was the scan rate,  $\Delta V$  was the potential window in the CV curves, and m was the mass loading of active materials on the electrodes.

The specific capacitance ( $C_p$ , mA h g<sup>-1</sup>) of positive electrode in three-electrode configuration was calculated according to the equation:

$$Cp = \frac{\mathbf{l} \cdot \Delta t}{m}$$
(2)

where I was the discharging current,  $\Delta t$  was the discharging time and m was the total mass of active materials.

The specific capacitance ( $C_c$ , mA h g<sup>-1</sup>) of Ni/Zn cells in twoelectrode configuration were calculated according to the equation:

$$Cc = \frac{\int I \cdot \Delta t}{M}$$
(3)

where I was the discharging current,  $\Delta t$  was the discharging time and M was the total mass of active materials on both cathode and anode.

Energy and power densities were calculated by using the following equations:

$$E = \int \frac{I \cdot V \cdot dt}{m}$$
(4)  
$$P = \frac{E}{\Delta t}$$
(5)

active electrode materials, and  $\Delta t$  was the discharging time.

### 3. Results and discussion

#### 3.1. Structural characterization of NNA@CNH and NNA@Zn nanostructured electrodes

The in situ electrodeposition method was employed to prepare CNH on NNA films; the mass loading of active materials and the degree of Co doping could be adjusted by tuning the deposition duration and modulating the Co<sup>3+</sup> ion concentration in the deposition bath. The SEM images of NNA@CNH are displayed in Fig. 2c, which revealed that CNH nanostructure was uniformly coated onto the Ni nanowires. As shown in Fig. S3 in the Supporting information, the mass loading of CNH could be conveniently tuned by adjusting the number of electrochemical deposition cycles. Transmission electron microscopy (TEM) images are displayed in Fig. 2d, which show that the nickel nanowires are uniformly coated with metal hydroxides with a thickness of about 30 nm. The magnified TEM image is shown in Fig. 2e, where no regular crystalline lattice was found in the Co-doped hydroxides, which was further verified by the XRD results (Fig. S4). The dopant of Co element was mapped by energy dispersive spectroscopy, where Co, Ni and O elements were all uniformly distributed around the Ni nanowires (Fig. 2f-i).

The chemical states of the bonded elements on the surface of the samples were identified by X-ray photoelectron spectroscopy (XPS) (Fig. 3). Fig. 3a displays the full spectrum of NNA@CNH sample, indicating the existence of Ni, Co and O elements, which confirms again that Co element was successfully incorporated in the nickel hydroxide domain. The O 1 s spectrum (Fig. 3b) shows

an O 1 s main peak centered at a binding energy of 531.3 eV, which could be assigned to bound hydroxide groups (OH<sup>-</sup>) revealing the formation of M–OH (M=Co, Ni) [16,17]. Furthermore, the broad peak contains a weak peak at 529.5 eV derived from absorbed water. The spectrum that was fit for Co 2p is shown in Fig. 3c. It consists of strong spin-orbit doublet peaks at 781.4 and 797.3 eV as well as shakeup satellite peaks at 787.3 and 803.6 eV, which are generally associated with Co<sup>2+</sup>, indicating the existence form of Co(OH)<sub>2</sub> [16]. The XPS spectra of Ni were analyzed using a similar fitting method. The results reveal that the peaks at binding energies of 856.0 eV and 873.8 eV can be assigned to  $Ni^{2+}$  [18,19]. Therefore, the formation of CHN can be confirmed from the above results of XPS studies. In order to have a clearer view of elemental distribution, the NNA@CNH sample was analyzed via XPS depth profile study. The depth profile analysis via X-ray sputtering on the NNA@CNH (prepared in 50 at% Co bath) was carried out as shown in Fig. S5. The Ni spectrum collected from different sputtering durations are displayed in Fig. S5a and b. The XPS depth profile experiment was carried out by scratching off the Ni@CNH nanowires from the substrate and compressing them into a sample pallet. The XPS spectra on Co and Ni elements were collected in every 20 s during the sputtering process, and Co/Ni content-depth information could be derived from the experiment. Briefly, Co/Ni content gradually decreased along with the sputtering duration, which statistically agreed well with the core-shell nanostructure feature (Fig. S5c). Moreover, NNA@CNH samples fabricated from electrodeposition bath with different Co at% were analyzed with their Co 2p spectrum. As shown in Fig. S5b, the sample derived from deposition bath with higher Co at% showed stronger intensity of Co 2p signal (Fig. S5d). Additionally, the correspondence between Co at% in the CNH composite and the electrodeposition bath are measured, as displayed in Fig. S6, which suggested that the Co content in NNA@CNH can be well controlled.

#### 3.2. Electrochemical properties of NNA@CNH cathode

The electrochemical properties of NNA@Ni(OH)<sub>2</sub> and NNA@CNH samples were investigated in a three-electrode configuration using 1 M KOH as electrolyte. The SCE was used as reference electrode and a piece of Pt foil was used as counter electrode. The electrochemical data were collected and analyzed in Fig. 4. In Fig. 4a, CV curves of both NNA@Ni(OH)<sub>2</sub> and NNA@CNH-1 (CNH sample derived from the deposition bath containing 10 at% of  $Co^{3+}$ ) at 1 mV s<sup>-1</sup> are displayed (the definition of CNH samples are listed in Table S1). The oxidation and reduction potential peaks of Ni(OH)<sub>2</sub> were observed at 0.36 V and 0.21 V (vs. SCE), respectively. This corresponds to the reversible reaction as below [11,20,21].

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
(6)

The cathodic and anodic peaks of NNA@Ni(OH)<sub>2</sub> consisted of two peaks within a broad shoulder. As compared, there was only one peak for NNA@CNH, which is in accordance with previous report [12]. The CV curves of NNA@CNH samples with different Co content are displayed in Fig. S7a, the oxidative and reductive peaks shifted negatively with the increment of Co% content in the samples. This can be contributed by the redox reactions derived from Co(OH)<sub>2</sub> (E=0.00 V vs. SCE for discharging process and E=0.05 V vs. SCE for charging process) [22]:

$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O + e^-$$
(7)

The position and strength of redox peaks are strongly related to the dopant concentration of Co, which well agrees with previous studies [23,24]. Also, the introduction of Co ions can effectively enlarge the closed area of the CV curves, suggesting improved



Fig. 3. Elements analysis. (a) XPS full spectrum of NNA@CHN. (b) O spectrum of NNA@CNH. (c) Co spectrum of NNA@CNH. (d) Ni spectrum of NNA@CNH.

specific capacitance. The relationship between the specific capacitance and various mass loadings of CNH samples is shown in Fig. S6b. The GCD experimental results of both NNA@Ni(OH)<sub>2</sub> and NNA@CNH-1 are displayed in Fig. 4b. The NNA@Ni(OH)<sub>2</sub> electrode showed a similar discharge plateau but had a lower capacity compared with NNAs@CNH-1 electrode, which was consistent with the CV analysis. The typical discharge curves of NNA@CNH-1 in various discharge current densities are displayed in Fig. 4c. A well-defined plateau for NNA@CNH-1 was observed, consistent with Eq. (6). The rate capabilities of the two samples were evaluated at current densities of 5, 10, 15–30 A  $g^{-1}$  sequentially. The average discharge capacities of NNA@CNH-1 were 346, 304, 242 and 158 mA h  $g^{-1}$  when tested at current densities of 5, 10, 15, and 30 A g<sup>-1</sup>, respectively. The NNA@Ni(OH)<sub>2</sub> electrode showed average discharge capacities of 272, 189, 150 and 99 mA h  $g^{-1}$  when tested at current densities of 5, 10, 15, and 30 A  $g^{-1}$ , respectively. We performed electrochemical measurements on NNAs@CNH-1 electrode at higher mass loading (up to  $4 \text{ mg cm}^{-2}$ ) and found that the capacity almost scaled up linearly to about  $1 \text{ mA h cm}^{-2}$ . The gravimetric specific capacitance decreased from 342 mA h  $g^{-1}$ to  $275 \text{ mA h g}^{-1}$  when the mass loading increased from  $0.49 \text{ mg cm}^{-2}$  to  $3.89 \text{ mg cm}^{-2}$ . The study on Co dopant is shown in Fig. S7, S8 and summarized in Table S1. Briefly, the NNA@CNH samples exhibited maximized specific capacitance of 2539 F  $g^{-1}$  at 1 mV s<sup>-1</sup>, where the Co at% content in the CNH is 44.5%. Moreover, the NNA@CNH samples exhibited superior cycling performance (11.5% capacitance loss after 5000 cycles for NNA@CNH-1) and

excellent capacitive performance ( $2270 \text{ F g}^{-1}$ ) with only a small amount of Co dopant (about 7.4 at%), as shown in Table S1 [12]. Therefore, the introduction of Co dopant into the amorphous Ni hydroxide is an effective way to improve the long-time cycle stability of the electrode.

Specifically, the charge-discharge cycling performance of NNA@Ni(OH)<sub>2</sub> and NNA@CNH-1 was evaluated at  $30 \text{ A g}^{-1}$ . NNA@CNH-1 showed superior cycling performance with about 90% capacitance retention after 5000 cycles, while NNA@Ni(OH)<sub>2</sub> only have 62.1% capacitance retention after 5000 cycles (Fig. 4f). To reveal the contribution of NNA nanostructure to the cycling performance, detailed experiments were carried out. Firstly, Ni foam (NF)@Ni(OH)<sub>2</sub> and NNA@Ni(OH)<sub>2</sub> samples with the same Ni(OH)<sub>2</sub> mass loading per electrode piece were cycled at 30 A  $g^{-1}$  under the GCD experimental condition (Fig. S8a). The NNA@Ni(OH)<sub>2</sub> maintained about 65% of its original capacitance while NF@Ni(OH)<sub>2</sub> maintained only about 20% of its original capacity (Fig. S9a), indicating the presence of NNA nanostructure can significantly improve the structural stability of the electrode. This can be further verified by the cycling performance results of NNA@CNH-1 and NF@CNH-1 (with the same specific mass loading by electrode dimension), as NNA@CNH-1 performed superior performance to the NF@CNH-1 (Fig. S9b). The GCD curves of NNA@CNH-1 on the 1st and 5000th cycles are displayed in Fig. S10. The morphological information of NNA@CNH-1 is displayed in Fig. S11, indicating insignificant structural damage of the sample after 5000 cycles in the GCD experiment. Additionally, the NNA



**Fig. 4.** Electrochemical measurements of NNA@CHN-1 cathode. (a) CV curves of NNA@CNH-1 and NNA@Ni(OH)<sub>2</sub>. (b) GCD curves of NNA@CNH-1 and NNA@Ni(OH)<sub>2</sub>, measured at 3 A  $g^{-1}$ . (c) GCD curves of NNA@CNH-1 at different current densities. (d) Rate performance of NNA@CNH-1 and NNA@Ni(OH)<sub>2</sub>. (e) The gravimetric and areal capacitance of NNA@CNH-1 electrode measured at the current density of 5 A  $g^{-1}$ . (f) Cycling performance of NNA@CNH-1 and NNA@Ni(OH)<sub>2</sub>.

and NF current collectors were loaded with CNH in approximately the same thickness via tuning the deposition cycles, and the NNA@CNH-1 electrode maintained higher capacitance retention than NF@CNH-1 (Fig. S12). The above cycling analysis revealed that both the introductions of NNA nanostructure and Co dopant contributed to the minimization of the capacitance loss on electrode materials. Based on the above discussion, NNA@CNH-1 sample was chosen as the positive electrode for the further study in Ni/Zn full cell.

Base on the above experimental results, both NNA nanostructure and Co-doping have contributed to the enhancement of the electrochemical performance of the cathode. Firstly, the NNA scaffold provided vertically-aligned fast electron and ion pathways for the active material, and the number of the electrochemically active sites is dramatically increased as well [15]. On the other hand, the Co–Ni(OH)<sub>2</sub> is deposited on the surface of NNA scaffold, which could effectively prevent the active materials from aggregation during the charge and discharge processes. Additionally, the surface convexity characteristic makes the NNA framework favorable to release electrostatic force caused by the electrochemical redox reactions during the cycling process [25]. While for the Co dopant, the charge and discharge of metal hydroxide electrode will cause repeated anisotropic electrostatic interactions between metal ions, which will induce distortions in the lattice and cause structural disintegration [16]. For the Co-doping electrodeposited samples, amorphous phases are characterized to be full of defects and long-range disorders, and thus the electrostatic interactions between metal ions are generally isotropically distributed, therefore, the structural distortions can be partially alleviated in the electrode [16].

Briefly, the excellent electrochemical performance of NNA@CNH electrode could be attributed by following factors: 1) the nickel nanowire forests help provide electron and ion "highways" with maximized surface areas, which are conducive to mass and charge transfer; 2) the surface convexity of the nickel nanowires contributes to release the stress generated by the cycling process of the electrode materials and thus can minimize the structural damages; 3) The increased level of defects and structural disorder introduced by Co dopant can further help minimize the stress during the repeated charge and discharge processes in the amorphous metal hydroxides [16,26].

#### 3.3. Device-level evaluation

As for the anode, the formation of Zn dendrites during repeated charge-discharge processes is detrimental to the stability of the Ni/ Zn battery [11]. To minimize the impact of dendrite formation on the capacity losses, intensive researches have been carried out, including separator modification, additives in the electrolyte, and pulsed charging [13,27]. Importantly, previous work highlighted that designing 3D current collector could suppress dendrites

growth [28]. Here, metallic nanowire array based anode is, for the first time, introduced to rechargeable Ni/Zn battery to minimize the capacity deterioration caused by dendrite formation. To make a fair evaluation about the NNA@Zn anode's contribution on the cell performance, Zn was deposited on both NNA film and conventional smooth Cu foil (control) via a directly electrochemical deposition process. The TEM and EDS-mapping images of NNA@Zn are carried out in Fig. S13, indicating the formation of the NNA@Zn core-shell nanostructure. Additionally, the XRD spectrum (Fig. S14) verified the electrodeposited Zn is well crystallized. The mass loading of Zn was controlled via tuning the cathodic deposition time to ensure the mass loading of Zn to be about 0.67 mg  $cm^{-2}$ [12]. Both NNA@Zn and Cu@Zn anodes were separately assembled into a full cell using NNA@CNH-1 as counter electrode with Codoped Ni(OH)<sub>2</sub> mass loading of about 1 mg cm<sup>-2</sup>. The measured specific capacity, energy density and power density were all normalized to the active materials, i.e. the total mass of CNH and Zn on two working electrodes for a fair comparison. The batteries showed an operating voltage of 1.7 V to 1.8 V, which corresponds to the reversible reaction [29]:

#### $2NiOOH+2H_2O+Zn\leftrightarrow Zn(OH)_2+2Ni(OH)_2$ E<sub>0</sub>=1.73 V (8)

The discharging voltage profiles of NNA@Zn based cell (NNA@Zn-cell) and Cu@Zn based cell (Cu@Zn-cell) are displayed in Fig. 5a. The NNA@Zn-cell showed higher discharge capacity than Cu@Zn-cell. This is probably because that NNA@Zn nanostructure can improve the contact between Zn and the substrate, as well as



Fig. 5. Electrochemical study on NNA@Zn-cell and Cu@Zn-cell. (a) The typical GCD curves of NNA@Zn-cell and Cu@Zn-cell. (b) Rate performance of NNA@Zn-cell and Cu@Zn-cell and Cu@Zn-cell. (c) EIS results of NNA@Zn-cell and Cu@Zn-cell. (d) Cycling performance of NNA@Zn-cell and Cu@Zn-cell.

the reactive Zn/electrolyte interfaces, thus enhancing the electrochemical efficiency of Zn anode under an adequate mass loading. Furthermore, specific capacitance based on the electrode mass of both NNA@Zn-cell and Cu@Zn-cell are displayed in Fig. 5b, which were measured under varied current densities ranging from 1 A  $g^{-1}$  to 8 A  $g^{-1}$ . The average discharge capacities of NNA@Zncell were 247, 234, 221 and 210 mA h  $g^{-1}$  at current densities of 1, 2, 4, and 8 A g<sup>-1</sup>. The Cu@Zn-cell showed average discharge capacities of 184, 170, 149, and 124 mA h g<sup>-1</sup> at current densities of 1, 2, 4, and 8 A g<sup>-1</sup>. This revealed that the NNA nanostructure can significantly contribute to the rate and capacitance performances of the Ni/Zn battery. Moreover, the NNA@Zn-cell showed  $R_e$  of 2.05  $\Omega$  and  $R_{ct}$  of 0.13  $\Omega$  while the Cu@Zn-cell showed  $R_e$  of 4.10  $\Omega$  and  $R_{ct}$  of 0.30  $\Omega$  (Fig. 5d), indicating that NNA@Zn-cell has a small



**Fig. 6.** Device-level evaluation on NNA@Zn-cell. (a) GCD curves of NNA based Ni/Zn alkaline battery. (b) GCD curves of NNA-Ni/Zn battery charged at 8 A  $g^{-1}$  and discharged at 1 A  $g^{-1}$ . (c) GCD curves of NNA@Zn-cell at bending/planar status. (d) The Ragone plot of the fabricated Ni/Zn alkaline batteries based on the mass of active materials on both electrodes. (e) A comparison on the cycling performance of NNA-based Ni/Zn aqueous battery with recently reported advanced alkaline batteries (the cycling experimental conditions are marked in the plots).

inner resistance and excellent ion diffusion capability.

We analyzed the cycling performance of NNA@Zn-cell and Cu@Zn-cell by GCD experiment under 8 A g<sup>-1</sup>. The capacity decay of NNA@Zn-cell was only ~ 10% after 5 000 cycles, while the Cu@Zn-cell lost 60% of its original capacity after 4000 cycles. The morphologies of NNA@Zn and Cu@Zn anode samples were analyzed after the cycling test. In Fig. S15, the formation of numerous Zn dendrites is very clear on the Cu@Zn film after the cycling process. However, there's no obvious dendrite formation on the NNA@Zn side, as only a small amount of ZnO was formed on the surface of the nanowires caused by repeatedly oxidation and reduction reactions on the electrode/electrolyte interface [12,13].

More specific electrochemical characterizations on NNA@Zncell is displayed in Fig. 6. The discharge voltage profiles of NNA@Zn-cell at various current densities ranging from  $1 \text{ Ag}^{-1}$  to  $8 \text{ Ag}^{-1}$  are displayed in Fig. 6a and the fully charge-discharge behavior profile is plotted in Fig. S16. At 1 A  $g^{-1}$ , the Ni/Zn battery delivered a high capacity of 247 mA h  $g^{-1}$  and maintained 210 mA h  $g^{-1}$  even at 8 A  $g^{-1}$ , in accordance with the excellent capacity and rate performance in Fig. 5b. We calculated the energy and power densities to obtain a Ragone plot (Fig. 6d) [9,12]. The NNA@Zn-cell delivered a peak energy density of 148.54 Wh kg<sup>-1</sup> at the power density of  $1725 \text{ W kg}^{-1}$ , and maintained 115 Wh kg<sup>-1</sup> at the power density of 138 000 W kg<sup>-1</sup>. The ultrafast charge feature of NNA@Zn-cell are revealed in Fig. 6b, as the Ni/Zn cell could be charged in about 51 s (at  $8 \text{ Ag}^{-1}$ ), and still presented high discharge energy density of  $138 \text{ Wh} \text{ kg}^{-1}$  and power density of 1 725 W kg<sup>-1</sup> at the discharge current of 1 A  $g^{-1}$ ). The maximized volumetric energy density of the device is  $4.05 \text{ Wh } \text{L}^{-1}$  with the corresponding power density of 47 kW L<sup>-1</sup>. The gravimetric energy and power densities based on the total mass of NNA and active materials, as well as volumetric energy density and power density are displayed in Fig. S17. The flexibility of full cell was evaluated via charging and discharging the NNA@Zn-cell at planar and bent status. The GCD curves (as shown in Fig. 6c) were slightly difference, indicating there was minor capacitance loss caused by the shape change of the flexible device. Also, the discharging plateau became insignificant at a high discharging current density (8 A  $g^{-1}$ ), which suggested that the diffusion limited redox reaction plays a dominant role at high rate in the aqueous battery [9,30]. Additionally, the cycling performance of NNA@CNH-1//NNA@Zn battery is displayed and compared with recent advanced aqueous alkaline battery devices [9,12,31,32], where the Ni/Zn battery based on our technology showed stable cycling performance up to 5000 cycles (with 88% capacitance retention) while most ever-reported advanced alkaline batteries could only cycle for less than 1000 cycles (detailed specific energy and cycling performance information are listed in Table S2). The safe, fast-charge, stable, high-energy and flexible characteristics make this NNA based rechargeable battery promising for next generation of energy storage devices.

#### 4. Conclusions

In summary, we designed and fabricated the flexible Ni/Zn aqueous battery by Co doping on the Ni(OH)<sub>2</sub> cathode and electrodeposition of Zn as the anode onto highly conductive, super-hydrophilic and flexible NNA film current collector. Both active materials were fabricated via simple one-step electro-deposition process. The as-fabricated NNA-based flexible Ni/Zn aqueous rechargeable battery can deliver high energy density (148.5 Wh kg<sup>-1</sup> at the power density of 1 725 W kg<sup>-1</sup>, and the corresponding volumetric energy density is 4.05 Wh L<sup>-1</sup>), fast-charge feature (charged within 1 min with negligible energy loss), excellent rate capability and cycling performance (up to 5000 cycles with  $\sim$ 12% capacity loss), which shows much better results than the prior arts in alkaline battery field. With the much elongated cycle life as well as superior energy and power densities, such technology could bridge the energy gap between electrochemical capacitors and thin film lithium ion batteries, which is a promising candidate for next generation of high performance miniaturized energy storage systems.

#### Acknowledgment

This work is financially supported by the National Key Basic Research Program of China (Project no. 2014CB932400), Guangdong Province Science and Technology Department (Project nos. 2014A010105002 & 2015A030306010), Hong Kong Government TRS Grant no. T23-407/13-N and Nanshan District "Rising Stars" (Project no. KC2014JSQN0010A) for financial supports.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.07.035.

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