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Regular Article

Wearable high-performance supercapacitors based on Ni-coated cotton textile with low-crystalline Ni-Al layered double hydroxide nanoparticles

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ABSTRACT

Wearable electronics are developing rapidly in recent years. In this work, we develop a cost-effective, facile, and scalable approach to transform insulating cotton textile to highly conductive Ni-coated cotton textile (NCT). In order to verify the feasibility of NCT as a flexible current collector for wearable supercapacitors, we electrodeposit low-crystalline Ni-Al layered double hydroxide (LDH) nanoparticles onto the NCT. The obtained NCT@NiAl-LDH shows high specific capacitance (935.2 mF cm⁻²), superior rate capability, and good cyclability. Besides, the asymmetric supercapacitor (ASC) assembled from NCT@NiAl-LDH exhibits high specific energy of 58.8 Wh kg⁻¹ (134 μ Wh cm⁻²) when the specific power is 539 W kg⁻¹ (1228 μ W cm⁻²). The results demonstrate great potential of our methodology.

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1. Introduction

The massive usage of fossil fuels has been causing serious consequences, *i.e.*, air pollution, global warming, and geopolitical

concerns. Therefore, it is emerging to develop high-performance electrochemical energy storage (EES) devices for renewable energy and electric vehicles, so as to reduce our dependence on fossil fuels [1]. Among various EES devices, electrical double-layer capacitors (EDLCs) are well-known for high specific power (~10 kW kg⁻¹) and extremely long life span (~100 thousand cycles) [2]. However, EDLCs suffer from low specific energy, which originates from their



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energy storage mechanism, i.e. surface-limited physical ion adsorption [3]. In contrast, pseudocapacitors deliver significantly higher specific energy than that of EDLCs, while their rate capability and cycling stability are much lower [4]. The mechanism behind that is pseudocapacitive materials (e.g., RuO₂, MnO₂, Co₃O₄, NiCo₂O₄, Ni(OH)₂, FeOOH, and MoS₂) store and release charges *via* surface and near-surface redox reactions [5–8]. Among various cathode materials for pseudocapacitors, metallic layered double hydroxides (LDHs) have proven to be highly promising, owing to intriguing layered structure, high redox activity, relatively low cost, and environmentally friendliness [9-12]. LDHs are a class of two-dimensional (2D) layered materials with a general formula of $[M_{1-x}^{II}M_{x}^{III}(OH)_{2}]^{x+}[A^{n-}]_{x/n} \cdot mH_{2}O$, where M^{II} and M^{III} are divalent and trivalent metal cations, and A^{n-} is the charge-balancing anion. Through varying M^{II} and M^{III}, different types of LDHs, such as Co-Ni LDHs [13], Co-Al LDHs [14], Ni-Mn LDHs [15], and Ni-Al LDHs [16], have been reported as high-performance pseudocapacitive materials. For instance, Li et al. used a homogeneous precipitation approach to obtain a nanocomposite comprised of NiAl-LDH and carbon nanotubes. Their product exhibited a high specific capacitance of 694 F g^{-1} at 1 A g^{-1} [17].

Nowadays, it is a trend to develop flexible, lightweight, and efficient EES devices, in order to satisfy the growing demands for wearable, portable, and smart electronics (e.g., roll-up displays, electronic papers, artificial biosensors, and implantable medical devices) [18–20]. Following this trend, several groups grew LDHs on flexible and conductive substrates, such as carbon cloth [21– 23], carbon paper [24], Cu-plated polyethylenterephthalate fibers [25], and reduced graphene oxide thin film [26]. For example, Yu et al. deposited CoNi-LDH nanosheets onto Ag nanowires-fenced carbon cloth, and realized large specific capacitance and high specific energy [22]. Despite great performances achieved by employing the above-mentioned substrates, these substrates are either expensive commercial products or unscalable. Herein, we choose cotton textile as the starting substance for constructing wearable supercapacitors because of its low cost, high flexibility. great strength, good breathability, abundance, renewability, and versatility. As cotton textile is made of cellulose fibers, it cannot be used as a current collector directly due to its insulation nature. To address this point, we introduce a cost-effective, facile, and scalable approach to coat Ni metal onto cotton textile, thus converting insulating cotton textile to conductive Ni-coated cotton textile (NCT). Moreover, this approach is applicable to all kinds of textiles. That is, the preparation of textile-based current collectors is highly tunable. In order to demonstrate the feasibility of NCT as a flexible current collector, we grow low-crystalline NiAl-LDH nanoparticles onto it. The resulting flexible electrode gives good performances in both three-electrode and two-electrode systems. In addition, our methodology can be extended to other pseudocapacitive materials. Therefore, this work offers a new platform in the advancement of wearable supercapacitors.

2. Experimental

2.1. Synthesis of NCT

Typically, cotton textile from a *T*-shirt was cut into $4 \times 6 \text{ cm}^2$ slices and immersed into aqueous sensitizing solution containing 0.05 M SnCl₂, 0.5 M HCl, and several Sn granules for 5 min. After rinsed with deionized water for 3 times, the cotton textile was immersed into aqueous activation solution containing 20 µg/mL PdCl₂ and 0.036 M HCl for 5 min, and was then rinsed with deionized water for 3 times. Subsequently, the cotton textile was immersed into aqueous electroless plating solution containing 0.0712 M NiSO₄, 0.561 M NH₄Cl, 0.034 M sodium citrate, and

0.283 M NaH₂PO₂ for 2 h. Before electroless plating, the pH of the solution was adjusted to 9–10 using concentrated ammonia water. After electroless plating, the cotton textile was rinsed by deionized water and ethanol for 3 times, and dried in air overnight. In order to further improve the electrical conductivity, electrodeposition was conducted on a CHI 660E electrochemical workstation using the Ni-plated cotton textile as the cathode, $2 \times 2 \text{ cm}^2$ Pt plate as the anode, and aqueous solution containing 0.15 M NiSO₄ and 0.12 M NH₄Cl as the electrolyte. After applying a constant voltage of 2.0 V for 8 min, the cotton textile was rinsed by deionized water and ethanol for 3 times, and dried in a vacuum oven overnight.

2.2. Synthesis of NCT@NiAl-LDH

NiAl-LDH was grown on the NCT through a standard threeelectrode set-up. NCT (pretreated with a dilute HCl solution), $2 \times 2 \text{ cm}^2$ Pt plate, and Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. NiAl-LDH was deposited on the surface of the NCT in an electrolyte composed of 0.1 M KNO₃, 0.075 M Ni(NO₃)₂ and 0.025 M Al(NO₃)₃ *via* a cyclic voltammetry (CV) method. The CV process was performed at 50 mV s⁻¹ for 20 cycles in the potential range of -1.25 to 0 V. After electrodeposition, the product was washed with deionized water and ethanol for 3 times, and finally dried in a vacuum oven overnight. The average mass loading of NiAl-LDH is 1.18 mg cm⁻².

2.3. Characterization and electrochemical measurements

X-ray diffraction (XRD) patterns were collected using a Rigaku RU300 diffractometer with Cu K α radiation source ($\lambda = 0.1540598$ nm). The morphology was recorded by a JEOL JSM-7600 field emission scanning electron microscope (FE-SEM). Investigation of the chemical compositions was performed using a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS). The ratio of Ni²⁺ to Al³⁺ was determined by a Varian VISTA-MPX inductively coupled plasma optical emission spectrometer (ICP-OES). Mechanical test was carried out on a tensile testing machine (Instron Model 5966) at a strain rate of 10 mm min⁻¹.

Three-electrode measurements were performed using NCT@NiAl-LDH, $2 \times 2 \text{ cm}^2$ Pt plate, Hg/HgO electrode, and 3 M KOH aqueous solution as the working electrode, counter electrode, reference electrode, and electrolyte, respectively. CV and galvanostatic charging/discharging (GCD) tests were conducted at different scan rates and current densities on a CHI 660E electrochemical workstation. Before the tests, the electrodes were pre-treated by CV scans at 50 mV s⁻¹ for 20 cycles. Electrochemical impedance spectroscopy (EIS) measurement was carried out with frequency ranging from 10 mHz to 100 kHz and the amplitude being set as 5 mV. For the two-electrode measurements, NCT@NiAl-LDH, NCT@G-Fe₂O₃, and polyvinyl alcohol (PVA)/KOH gel served as the positive electrode, negative electrode, and electrolyte, respectively. The synthesis process of G-Fe₂O₃ can be found in our previous report [27]. The NCT@G-Fe₂O₃ electrode was prepared by mixing G-Fe₂O₃ with polyvinylidene difluoride (PVDF) and Super P (conductive carbon black) at a weight ratio of 8:1:1 in Nmethylpyrrolidone (NMP) and then pasting the slurry onto one side of NCT, followed by vacuum drving at 100 °C for 12 h. The preparation of PVA/KOH gel electrolyte and the assembly of solid-state asymmetric supercapacitor (ASC) device were similar to our previous report [28]. Typically, 2 g PVA and 2 g KOH were added to 20 mL deionized water, followed by heating at 85 °C under vigorous stirring until the solution became clear. The obtained viscous solution was dropped onto NCT@NiAl-LDH and NCT@G-Fe₂O₃, and then these two electrodes were assembled together. After the electrolyte solidified to a gel, the two electrodes were further pressed to form a flexible solid-state ASC.

3. Results and discussion

The synthesis process of NCT@NiAl-LDH is schematically illustrated in Fig. 1a. First, cotton textile was transformed into NCT through electroless plating and subsequent electrodeposition. This transformation was accompanied by the color change from white to grey black. In addition, it can be seen that the NCT is comprised of inter-connected fibers, implying that Ni is uniformly coated on cotton fibers. Thanks to uniform Ni coating, the electrical conductivity of NCT was measured to be 1.43×10^4 S m⁻¹, which is high enough as a current collector. NCT was then used as the substrate for the electrodeposition of NiAl-LDH. During electrodeposition, NO₃ in the electrolyte accepted electrons from the NCT and was reduced to OH⁻. Subsequently, the accumulation of OH⁻ in the local region led to the co-deposition of hydroxides on the surface of NCT. As is shown by the photographs, the surface color of NCT turned from grey black into aqua green after electrodeposition, suggesting the successful growth of NiAl-LDH on Ni-coated cellulose fires. Besides, the obtained NCT@NiAl-LDH has great mechanical properties, i.e. good flexibility and high tensile strength of 3.91 GPa (Fig. S1). The SEM images of NCT@NiAl-LDH are shown in Fig. 1b-d. Fig. 1b reveals that NCT@NiAl-LDH inherits the fiber morphology from NCT. Fig. 1c indicates that NiAl-LDH is homogeneously deposited on Ni-coated cellulose fibers with a dense packing. Higher magnification image in Fig. 1d demonstrates that NiAl-LDH consists of nanoparticles with an average size of \sim 40 nm. Such nanoscaled structure could increase redox reaction sites and facilitate charge transports [29,30].

Fig. 2a shows XRD patterns of NCT@NiAl-LDH. The broad peak at around 45° is ascribed to the (1 1 1) plane of face-centered cubic Ni (JCPDS 04-0850), while the other small peaks are mainly attributed to P and NiAl-LDH. However, the peaks arising from NiAl-LDH are too low to be clearly identified. To solve this problem, neat

NiAl-LDH powder was carefully scraped from the NCT substrate and its XRD pattern is also shown in Fig. 2a. It exhibits a series of diffraction peaks that can be indexes as (0 0 3), (0 0 6), (0 1 2), (0 1 5), (0 1 8), (1 1 0), (1 1 3), and (2 0 2) planes of NiAl-LDH, similar to hydrotalcite-like LDH phase (JCPDS 15-0087). In addition, these peaks are very broad, suggesting that the obtained NiAl-LDH has rather low crystallinity. In low-crystalline pseudocapacitive materials, sufficient structural defects and disorder can facilitate the diffusion/reaction of electrolyte ions, while isotropic strain and stress upon charging/discharging are beneficial to the long-term electrochemical stability. Therefore, low-crystalline metal oxide and hydroxide materials are capable of achieving better performances than the high-crystalline counterparts [30–33].

XPS measurement was carried out to determine the chemical contents and valence states of NCT@NiAl-LDH, as shown in Fig. 2b-d. The survey XPS spectrum in Fig. 2b considerably resembles that of a previously reported NiAl-LDH [34]. The existence of C element in NCT@NiAl-LDH originates from surface adsorption and contamination [35]. The high-resolution O 1 s spectrum in the inset of Fig. 2b exhibits a strong peak centered at 531.8 eV, which is associated with bound hydroxide groups (OH⁻) [36]. In Fig. 2c, the high-resolution Ni 2p spectrum can be deconvoluted into two spin-orbit doublets at 874.1 eV (Ni 2p1/2) and 856.4 e V (Ni $2p_{3/2}$) with a spin-energy separation of 17.7 eV, as well as two shake-up satellites at 880.2 and 862.2 eV, which are in good agreement with Ni²⁺ [34,37,38]. Fig. 2d shows two peaks at 119.2 and 74.4 eV, relating to Al 2 s and Al 2p of Al³⁺, respectively [34,39]. According to ICP-OES analysis, the atomic ratio of Ni²⁺ to Al³⁺ is 1.38:1 in the NiAl-LDH.

Fig. 3a presents CV curves of NCT@NiAl-LDH at different scan rates. These curves demonstrate quite different profiles from the ideal rectangular shape of EDLCs, indicating that the charge storage within NiAl-LDH is dominated by the Faradaic redox reaction as follows

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
(1)



Fig. 1. (a) Schematic illustration of the fabrication process and (b, c, d) SEM images of NCT@NiAl-LDH.



Fig. 2. (a) XRD patterns of NCT@NiAl-LDH and neat NiAl-LDH powder scraped from the NCT substrate. (b) Survey, (c) Ni 2p high-resolution, and (d) Al 2 s and Al 2p high-resolution XPS spectra of NCT@NiAl-LDH.

At 5 mV s⁻¹, the anodic and cathodic peaks of NCT@NiAl-LDH are located at 0.581 and 0.415 V, respectively, with the peak separation being merely 0.166 V. When the scan rate is increased to 10, 20, 30, and 50 mV s⁻¹, the anodic peak becomes indistinct, while the cathodic peak shifts to 0.404, 0.393, 0.386, and 0.380 V, respectively. This phenomenon results from aggravated electrochemical polarization at higher scan rates [27,28]. As is shown in Fig. 3b, sloped charging and discharging plateaus dominate the GCD curves of NCT@NiAl-LDH, in good line with the CV curves. The rate-dependent specific capacitances of NCT@NiAl-LDH are summarized in Fig. 3c. According to CV curves, NCT@NiAl-LDH delivers 935.2 mF cm⁻² (792.5 F g^{-1}) and 311.9 mF cm⁻² (264.3 F g^{-1}) at 5 and 50 mV s^{-1} , respectively. The specific capacitances calculated from GCD curves are generally lower than that calculated from CV curves. At 1 mA cm⁻². NCT@NiAl-LDH exhibits discharging capacitance of 908 mF cm⁻², which is higher than many recently reported metal hydroxides. such as Ni-Co-Fe hydroxides (420 mF cm⁻²) [32], Ni(OH)₂ (70.6 mF cm⁻²) [40], NiAl-LDH (678 mF cm⁻²) [41], NiMn-LDH (670 mF cm⁻²) [42], CoAl-LDH (516 mF cm⁻²) [43], and NiCo-LDH (632 mF cm^{-2}) [25].

The electrochemical behavior of NCT@NiAl-LDH was further investigated by EIS measurement, and the obtained Nyquist plots are shown in Fig. 4a. The intercept of the high frequency region with the real axis represents the bulk resistance *Rs*, while the depressed semicircle at middle frequency reflects the charge transfer impedance *Rct*. In the low frequency domain, the 67° inclined line implies the combination of surface-related and diffusion-controlled charge storage mechanisms. The Nyquist plots were fitted using the equivalent circuit in the inset of Fig. 4a, in which $C_{\rm p}$, $R_{\rm l}$, $C_{\rm dl}$, and *W* account for pseudocapacitance, leakage resistance in parallel with $C_{\rm p}$, electrical double layer element, and Warburg impedance (diffusive impedance), respectively. Herein, the low values of *R*ct (4.48 Ω) and *W* (9.80 Ω s^{-1/2}) are indicative of favorable charge transfer kinetics and fast charge transports. Cyclability is also an important parameter for electrode materials. Fig. 4b shows the cycling performance of NCT@NiAl-LDH tested at 50 mV s⁻¹. The specific capacitance declines fast in initial 500 cycles due to inevitable strain/stress associated with the redox reaction, and then declines very slowly. After 5000 cycles, 75.2% of the initial capacitance can be maintained.

To further evaluate NCT@NiAl-LDH, it was used as the positive electrode for assembling a solid-state ASC device. In addition to NCT@NiAl-LDH, NCT@G-Fe₂O₃ and PVA/KOH were used as the negative electrode and gel electrolyte, respectively. Prior to the assembly of ASC device, the mass of NiAl-LDH and G-Fe₂O₃ was balanced according to: $q_+ = q_-$. From the CV curve of NCT@G-Fe₂O₃ in Fig. 5a, it can be determined that the specific capacitance of G-Fe₂O₃ is 599.6 C g⁻¹ at 5 mV s⁻¹. Given that NiAl-LDH delivers 475.5 C g⁻¹ at 5 mV s⁻¹ with a mass loading of 1.18 mg cm⁻², we chose 0.9 to 1.0 mg cm⁻² as the mass loading for NCT@G-Fe₂O₃. Because of the compatible potential windows of NiAl-LDH and G-Fe₂O₃, the ASC can give a high open-circuit voltage of 1.7 during CV measurement, as shown in Fig. 6a. As water splitting is more severe during GCD tests, the potential cutoffs were 0.55 and -1.05 V vs. Hg/HgO for NiAl-LDH upon charging (see Fig. 3b) and G-Fe₂O₃ upon



Fig. 3. (a) CV curves, (b) GCD curves, and (c) rate-dependent specific capacitances of NCT@NiAl-LDH.



Fig. 4. (a) Nyquist plots and (b) cycling performance of NCT@NiAl-LDH.

discharging (see our previous report [27]), respectively. Therefore, we chose 1.6 V as the voltage cutoff for the ASC device under GCD tests. Besides, GCD measurements were carried out based on the total mass of NiAl-LDH and G-Fe₂O₃. The obtained GCD curves in Fig. 5b are nonlinearly correlated with the potential, indicative of pseudocapacitive behavior. As the current density increases from 0.5 to 5 A g⁻¹, the discharging capacitance of the ASC decreases from 151.1 to 50.4 F g⁻¹.

Specific energy and specific power are two crucial factors for ASC devices. Fig. 5c displays gravimetric Ragone plots of our ASC compared with recently reported LDH-based ASCs [16,26,34,37,42–49]. The maximum specific energy of our ASC is 58.8 Wh kg⁻¹ at a specific power of 539 W kg⁻¹, while it maintains

15.2 Wh kg⁻¹ at 4172 W kg⁻¹. Impressively, the energy-power performance of our ASC is superior to most of these advanced LDH-based ASCs, suggesting great promise of the ASC configuration proposed in the present study. Moreover, it is worth mentioning that the areal energy density of our ASC (134 μ Wh cm⁻² at 1228 μ W cm⁻²) surpasses many recently reported ASCs, such as Ni_{0.67}Co_{0.33} LDH-based ASC (78.8 μ Wh cm⁻² at 785 μ W cm⁻²) [22] and Ag₃O₄-grafted NiO-based ASC (74 μ Wh cm⁻² at 998 μ W cm⁻²) [50]. Fig. 5d shows the cycling performance of our ASC at 100 mV s⁻¹. The capacitance decreases relatively rapidly in the initial 1000 cycles, after which only slight capacitance dropping can be observed. After 5000 cycles, the ASC maintains 70.7% of its initial capacitance.



Fig. 5. (a) CV curves of NCT@G-Fe₂O₃ and NCT@NiAl-LDH at 5 mV s⁻¹, and NCT@NiAl-LDH//NCT@G-Fe₂O₃ ASC at 10 mV s⁻¹. (b) GCD curves of the ASC device. (c) Ragone plots of our ASC device compared with recently reported LDH-based ASCs. (d) Cycling performance of our ASC device.

4. Conclusions

In summary, we propose a new methodology using cotton textile as the starting substance for the assembly of wearable supercapacitors. The insulating cotton textile is converted to highly conductive NCT by the combination of electroless plating and electrodeposition of metal Ni. This approach is applicable to almost all kinds of textiles. By using an electrodeposition method, we grow low-crystalline NiAl-LDH nanoparticles onto the NCT. The obtained flexible NCT@NiAl-LDH electrode delivers high specific capacitances of 935.2 and 311.9 mF cm⁻² at 5 and 50 mV s⁻¹, respectively, together with good capacitance retention of 75.2% after 5000 cycles under three-electrode measurements. In addition, a solidstate ASC device assembled from NCT@NiAl-LDH achieves high specific energy (58.8 Wh kg⁻¹ and 134 μ Wh cm⁻²). The methodology in this work can be extended to other energy storage materials. Thus this work provides a general, cost-effective, and scalable route to wearable energy-storage devices.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2017.11.046.

References

[1] H.S. Kim, J.B. Cook, H. Lin, J.S. Ko, S.H. Tolbert, V. Ozolins, B. Dunn, Nat. Mater. 16 (2017) 454–460.

- [2] F. Beguin, V. Presser, A. Balducci, E. Frackowiak, Adv. Mater. 26 (2219–2251) (2014) 2283.
- [3] P. Simon, Y. Gogotsi, B. Dunn, Science 343 (2014) 1210–1211.
- [4] L. Shen, L. Yu, H.B. Wu, X.Y. Yu, X. Zhang, X.W. Lou, Nat. Commun. 6 (2015) 6694.
- [5] Y. Yang, H. Fei, G. Ruan, C. Xiang, J.M. Tour, Adv. Mater. 26 (2014) 8163–8168.
 [6] F. Liu, H. Su, L. Jin, H. Zhang, X. Chu, W. Yang, J. Colloid Interf. Sci. 505 (2017) 796–804.
- [7] C. Wei, Y. Huang, M. Chen, J. Yan, W. Yao, X. Chen, J. Colloid Interf. Sci. 504 (2017) 1–11.
- [8] Y. Wei, R. Ding, C. Zhang, B. Lv, Y. Wang, C. Chen, X. Wang, J. Xu, Y. Yang, Y. Li, J. Colloid Interf. Sci. 504 (2017) 593–602.
- [9] L. Lv, K. Xu, C. Wang, H. Wan, Y. Ruan, J. Liu, R. Zou, L. Miao, K. Ostrikov, Y. Lan, J. Jiang, Electrochim. Acta 216 (2016) 35–43.
- [10] X. Li, J. Zai, Y. Liu, X. He, S. Xiang, Z. Ma, X. Qian, J. Power Sources 325 (2016) 675–681.
- [11] Z. Li, M. Shao, L. Zhou, R. Zhang, C. Zhang, J. Han, M. Wei, D.G. Evans, X. Duan, Nano Energy 20 (2016) 294–304.
- [12] J. Hao, W. Yang, Z. Zhang, B. Lu, X. Ke, B. Zhang, J. Tang, J. Colloid Interf. Sci. 426 (2014) 131–136.
- [13] J.H. Lee, H.J. Lee, S.Y. Lim, K.H. Chae, S.H. Park, K.Y. Chung, E. Deniz, J.W. Choi, Adv. Funct. Mater. 27 (2017) 1605225.
- [14] X. Wu, L. Jiang, C. Long, T. Wei, Z. Fan, Adv. Funct. Mater. 25 (2015) 1648–1655.
 [15] M. Li, F. Liu, X.B. Zhang, J.P. Cheng, Phys. Chem. Chem. Phys. 18 (2016) 30068–
- 30078.
- [16] X. Ge, C. Gu, Z. Yin, X. Wang, J. Tu, J. Li, Nano Energy 20 (2016) 185–193.
- [17] C. Bai, S. Sun, Y. Xu, R. Yu, H. Li, J. Colloid Interf. Sci. 480 (2016) 57–62.
- [18] L. Kou, T. Huang, B. Zheng, Y. Han, X. Zhao, K. Gopalsamy, H. Sun, C. Gao, Nat. Commun. 5 (2014) 3754.
- [19] Z. Chai, N. Zhang, P. Sun, Y. Huang, C. Zhao, H.J. Fan, X. Fan, W. Mai, ACS Nano 10 (2016) 9201–9207.
- [20] X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, Z.L. Wang, Adv. Mater. 28 (2016) 98–105.
- [21] Y. Liu, N. Fu, G. Zhang, M. Xu, W. Lu, L. Zhou, H. Huang, Adv. Funct. Mater. 27 (2017) 1605307.
- [22] S.C. Sekhar, G. Nagaraju, J.S. Yu, Nano Energy 36 (2017) 58-67.
- [23] T. Wang, S. Zhang, X. Yan, M. Lyu, L. Wang, J. Bell, H. Wang, A.C.S. Appl, Mater. Interf. 9 (2017) 15510–15524.
- [24] X. Wang, X. Li, X. Du, X. Ma, X. Hao, C. Xue, H. Zhu, S. Li, Electroanalysis 29 (2017) 1286–1293.
- [25] G. Nagaraju, G.S. Raju, Y.H. Ko, J.S. Yu, Nanoscale 8 (2016) 812-825.
- [26] R. Zhang, H. An, Z. Li, M. Shao, J. Han, M. Wei, Chem. Eng. J. 289 (2016) 85–92.
- [27] J. Chen, J. Xu, S. Zhou, N. Zhao, C.-P. Wong, Nano Energy 15 (2015) 719–728.
- [28] J. Chen, J. Xu, S. Zhou, N. Zhao, C.-P. Wong, J. Mater. Chem. A 3 (2015) 17385– 17391.

- [29] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong, Y. Li, Adv. Mater. 25 (2013) 267-272.
- [30] J. Chen, J. Xu, S. Zhou, N. Zhao, C.-P. Wong, Nano Energy 21 (2016) 145–153.
 [31] H.B. Li, M.H. Yu, F.X. Wang, P. Liu, Y. Liang, J. Xiao, C.X. Wang, Y.X. Tong, G.W.
- Yang, Nat. Commun. 4 (2013) 1894.
- [32] H.B. Li, Y.Q. Gao, C.X. Wang, G.W. Yang, Adv. Energy Mater. 5 (2015) 1401767. [33] K.A. Owusu, L.B. Qu, J.T. Li, Z.Y. Wang, K.N. Zhao, C. Yang, K.M. Hercule, C. Lin, C.
- W. Shi, Q.L. Wei, L. Zhou, L.Q. Mai, Nat. Commun. 8 (2017) 14264. [34] S.X. Wu, K.S. Hui, K.N. Hui, K.H. Kim, A.C.S. Appl, Mater. Interf. 9 (2017) 1395-
- 1406. [35] J. Chen, X. Zhou, C. Mei, J. Xu, S. Zhou, C.-P. Wong, Electrochim. Acta 222 (2016)
- 172–176. [36] F. Ning, M. Shao, C. Zhang, S. Xu, M. Wei, X. Duan, Nano Energy 7 (2014) 134-
- 142.
- [37] F. Lai, Y.E. Miao, L. Zuo, H. Lu, Y. Huang, T. Liu, Small 12 (2016) 3235-3244.
- [38] J. Xu, Z. Ju, J. Cao, W. Wang, C. Wang, Z. Chen, J. Alloys Compd. 689 (2016) 489-499.
- [39] X.Q. Ji, W.L. Zhang, L. Shan, Y. Tian, J.Q. Liu, Sci. Rep. 5 (2015) 18367.
 [40] Y. Yang, L. Li, G.D. Ruan, H.L. Fei, C.S. Xiang, X.J. Fan, J.M. Tour, ACS Nano 8 (2014) 9622-9628.

- [41] M. Liu, S. He, Y.-E. Miao, Y. Huang, H. Lu, L. Zhang, T. Liu, RSC Adv. 5 (2015) 55109-55118.
- [42] X.L. Guo, X.Y. Liu, X.D. Hao, S.J. Zhu, F. Dong, Z.Q. Wen, Y.X. Zhang, Electrochim. Acta 194 (2016) 179-186.
- [43] X. Liu, A. Zhou, T. Pan, Y. Dou, M. Shao, J. Han, M. Wei, J. Mater. Chem. A 4 (2016) 8421-8427.
- [44] X. Bai, Q. Liu, H. Zhang, J. Liu, Z. Li, X. Jing, Y. Yuan, L. Liu, J. Wang, Electrochim. Acta 215 (2016) 492-499.
- [45] M. Li, J.P. Cheng, J. Wang, F. Liu, X.B. Zhang, Electrochim. Acta 206 (2016) 108-115
- [46] L. Zhang, K.N. Hui, K. San Hui, H. Lee, J. Power Sources 318 (2016) 76-85.
- [47] Z. Gao, C. Bumgardner, N. Song, Y. Zhang, J. Li, X. Li, Nat. Commun. 7 (2016) 11586.
- [48] P.F. Liu, J.J. Zhou, G.C. Li, M.K. Wu, K. Tao, F.Y. Yi, W.N. Zhao, L. Han, Dalton T. 46 (2017) 7388-7391.
- [49] Y. Lu, B. Jiang, L. Fang, F. Ling, F. Wu, B. Hu, F. Meng, K. Niu, F. Lin, H. Zheng, J. Alloys Compd. 714 (2017) 63-70.
- [50] I.M. Babu, K.K. Purushothaman, G. Muralidharan, J. Mater. Chem. A 3 (2015) 420-427.