

Pseudocapacitors

An Ultralong, Highly Oriented Nickel-Nanowire-Array Electrode Scaffold for High-Performance Compressible

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With the bloom of portable electronics,^[1,2] the development of ultrathin, flexible, and high-performance energy-storage devices has been attracting more attention than ever. As compared with other secondary energy-storage devices, e.g., lithium-ion batteries, supercapacitors are featured with faster charge-discharge rates and much higher longevity. Even so, current miniaturized supercapacitor technology still faces the challenge of increasing both the energy and power densities, which can potentially be overcome by building efficient 3D electrode architectures.^[3,4] As for the electrode materials, transitionmetal oxides and conductive polymers have been considered as superior alternative active materials to the conventional carbon materials since they can provide 10-100 times greater energy density due to the pseudocapacitive characteristic.^[5,6] However, their poor electrical conductivity and cyclability have been hindering their wider energy-storage applications.^[5,7,8] Therefore, more and more attention has been attracted to the rational design of the electrodes with 3D hierarchical structure, which can not only improve the charge and mass transport with a high-electrode active materials loading but also help to release the stress caused during electrochemical cycling, thus helping improve the device performances.

Previous studies primarily focused on the deposition of active materials on a reticular or porous conductive scaffold.^[9,10] Nanocarbon materials have been widely considered as excellent conductive frameworks for pseudocapacitive materials,^[11,12] yet the large contact resistance between interfaces and the tortuous structure are inefficient for charge and mass transfer. Moreover, the hydrophobic nature of highly graphitized carbon is adverse for soaking the electrolyte.^[11,13] As compared, metallic

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mechanical property.^[6,14] Besides, coupling the 3D electrode skeletons with electrochemically active materials can render excellent capacitive property.^[6,14–16] For example, ZnO-nanopillar-array-supported nanoscaled MnO₂ was developed.^[17] Su et al. investigated the electrochemical properties of the Ninanocone-array@MnO₂ nanostructured ultrathin electrodes.^[11] Yu et al. printed well-ordered polyacrylonitrile nanopillars and deposited Au-Pd layer and MnO₂ on top of the electrodes.^[18] Additionally, the rational design of hierarchical structures of the electrode can also cater to the development of other energy devices such as the quantum dot sensitized solar cells and micro-lithium-ion batteries, which largely rely on the charge transfer and storage process.^[19,20] Here, we have prepared, for the first time, a vertically pliqued Ni nanowire array (NNA) with diameter ranging from

conductive skeletons, such as nickel-based ones, could be more

competitive due to its intrinsic hydrophic nature, excellent ohmic conductance in the whole electrode as well as superior

aligned Ni nanowire array (NNA) with diameter ranging from 120 to 170 nm and length up to 1 mm as the electrode scaffold, followed by electrodepositing MnO2 as the cathode and polypyrrole (PPy) as the anode for an aqueous asymmetric micro-supercapacitor. As shown in Figure 1, the NNA was formed through a modified magnetic-field-driven selectivedeposition growth process.^[14] Different from previous studies, the NNA is metallurgically bonded to the substrate film via Pd nanoparticles interlayer through cold welding where the Pd active layer demonstrated a good contact with Ti substrate as displayed in Figure S1 (Supporting Information). This is due to the giant magnetic moment of Pd nanoparticles that can strengthen the adhesion between Ni and Ti (Figure S2 and S5, Supporting Information).^[11,21-23] In this work, ultralong nanowire arrays rather than shorter ones were employed as the scaffolds for both MnO₂ and PPy; this is due to the fact that NNA with higher aspect ratio can provide more nickel/active materials active sites and reduce the thickness of active materials under the same mass loading. A smaller thickness of the active materials eventually contributes to faster charge transfer and a superior electrochemical performance. The as-prepared NNA serves as essential electrical and mechanical support for both MnO₂ and PPy. Subsequently, the two electrodes are separated by a commercial separator and integrated into an aqueous cell, which can deliver superior energy and power densities with outstanding cycle stability. Furthermore, it exhibits excellent flexibility and compressibility characteristics.

As shown in **Figure 2**a, Ni nanowires with the diameter of 120–170 nm and aspect ratio of over 8000 were uniformly deposited on the substrate. The morphological features of the

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Figure 1. Schematic illustration of the fabrication process. A piece of Ti foil is activated by depositing Zn and Pd, and then NNA is grown onto the activated Ti foil by applying magnetic field in vertical direction. Subsequently, PPy and MnO_2 were deposited on the NNA samples for electrodes. Finally, the electrodes are compressed and assembled into an ASC with aqueous electrolyte.

NNA could be controlled by adjusting the deposition parameters (Figure S2 and S3, Supporting Information). We also investigated the specific surface area of the NNA combining modeling calculation and Brunauer–Emmett–Teller (BET) measurement (Figure S6, Supporting Information). The BETmeasured specific surface area of the NNA nanostructure was 2.10 m² g⁻¹, which well matched with the calculated results (2.29 m² g⁻¹). The contact angle test (Figure S7, Supporting Information) indicates the NNA film is superhydrophilic. The adhesion between NNA and the substrate was verified by tape test and pressing test, where negligible loss of structural integrity of the NNA was found (Figure S8, Supporting Information); additionally, both the calculation and measurement results about specific surface area were compared (Figure S6 and S8; Table S1 and S2, Supporting Information).^[24]

To prepare the NNA@ MnO_2 cathode, a layer of nanostructured MnO_2 was uniformly deposited onto the NNA via electrodeposition (Figure 2b). Figure 2c shows the transmission electron microscopy (TEM) image of a single piece of typical nanowire sample of NNA@MnO₂; the Ni nanowires are epitaxially covered by the MnO2 with a featured thickness of \approx 40 nm, and the Mn and O elements are found to be uniformly distributed via energy dispersive spectroscopy mapping.^[11] The magnified TEM image of MnO₂ suggests that the electrodeposited MnO₂ is amorphous, as no ordered lattice was detected.^[11] This was further certified by the fast Fourier transform (FFT) (Figure 2d, inset) and X-ray diffraction characterization (Figure S10, Supporting Information). The valence state of the electrodeposited MnO2 on NNA was investigated by X-ray photoelectron spectroscopy (XPS). The XPS full spectrum (Figure S11a, Supporting Information) contains signals from Mn, O, and Ni elements. The Mn $2p_{3/2}$ and Mn $2p_{1/2}$ have binding energy located at 641.62 and 653.82 eV, respectively (Figure S11b, Supporting Information). The separation of two



Figure 2. SEM side view images of a) NNA and b) NNA@MnO₂; TEM images of c) NNA@MnO₂ with low magnification and d) NNA@MnO₂ with high magnification (inset image: FFT diffraction of the MnO₂ region).



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binding energy peaks is 12.20 eV, which is highly consistent with previous reports.^[25,26] In addition, the binding energy separation (ΔE_b) between two peaks of Mn 3s component can be used to identify the oxidation state of Mn in manganese oxides. Here, the ΔE_b is 4.99 eV, located between 4.80 eV (Mn⁴⁺) and 5.30 eV (Mn³⁺), in good accordance with previous report.^[25] Additionally, the O 1s spectrum was also analyzed. Importantly, the valence of Mn is consistent with the analytical result of the Mn 3s spectrum.^[26] The structural characteristics of the NNA@PPy were studied as well (Figure S12–S14, Supporting Information).

The electrochemical performance of the NNA@MnO2 electrode was evaluated with a three-electrode configuration in Na_2SO_4 (0.5 M) aqueous solution, where Pt foil was employed as the counter electrode, saturated calomel electrode as the reference electrode, and a piece of NNA@MnO₂ as the working electrode. It is worth to be noted that both the mass loading positive and negative electrode active materials are calculated via charge flow throughout the electrodeposition process, which is higher than actual mass loading due to electron loss.^[27] Figure 3a demonstrates the cyclic voltammetry (CV) curves of the NNA@MnO2 and NF (nickel foam) $@MnO_2$ at the same mass loading of 3.51 mg cm⁻². The corresponding specific mass and areal capacitances of NNA@MnO2 are 214 F g⁻¹ and 750 mF cm⁻² (1 mV s⁻¹), respectively; as compared, the NF@MnO₂ sample (the specific surface area of NF is $\approx 0.16 \text{ m}^2 \text{ g}^{-1}$) only shows a specific capacitance of 135.1 F g^{-1} at 1 mV s^{-1} . Figure 3b manifests the galvanostatic charging/discharging (GCD) curves of NNA@MnO2, which are nearly triangular and exhibit a minimized IR drop of 0.023 V (0.5 mA cm⁻²). Meanwhile, the NNA@MnO2 electrode presents a smaller IR drop and higher capacity than NF@ MnO_2 at 1 mA cm⁻² (Figure 3c). This result was further demonstrated by the Nyquist plots of the electrochemical impedance spectroscopy (EIS) analysis (Figure 3d). The impedance data was fitted into an equivalent electrical circuit (Figure S15, Supporting Information) consisting of the electrolyte resistance (R_e) and charge transfer resistance (R_{ct}). Via a complex nonlinear least-squares fitting, the R_e/R_{ct} of NNA@MnO₂ is 12.30/3.76 Ω as compared with 12.75/9.77 Ω of NF@MnO₂. The similar R_e suggests that the electron transport of NNA is as good as NF, while the smaller R_{ct} indicates that NNA has a superior electron transportation and higher surface area. This was proven by the Bode phase plots of NNA@MnO₂ and NF@MnO₂ where the NF@MnO₂ showed a larger corresponding time constant τ_0 (Figure 3e).^[28]

It is noteworthy that NNA@MnO2 demonstrates excellent cycling performance with 103.7% capacitance retention after 20 000 cycles (Figure 3f), while the NF@MnO2 electrode shows inferior cycle stability such that only $\approx 20\%$ of its original capacitance can be retained after 5000 cycles (Figure S16, Supporting Information); the areal-capacitance-based cycling performance and GCD results of NNA@MnO2 are displayed in Figure S17 (Supporting Information). Furthermore, the NF@ MnO₂ and the NNA@MnO₂ samples with the same thickness (\approx 50 nm) of MnO₂ were prepared. The capacitance retention of this NF@MnO2 is 20% after 15 000 cycles (Figure S18, Supporting Information). TEM analysis (Figure S19, Supporting Information) suggests that the NF@MnO2 suffers from severe structural damage during the charge-discharge process, which leads to capacitance loss. Moreover, the corresponding electrochemical performance of the NNA@MnO2 and NNA@PPy film after the pressing test was studied (Figure S20, Table S3 and S4, Supporting Information). After pressing, the volume of the electrodes decreased by about four times with negligible energy loss. Meanwhile, the comparison of the electrochemical performance of NNA@MnO2 with recently reported advanced MnO2-based microstructures is given (Table S7, Supporting Information).



Figure 3. a) CV curves of bare NNA, NNA@MnO₂, and NF@MnO₂ at 1 mV s⁻¹. b) GCD curves of NNA@MnO₂. c) GCD curves of NNA@MnO₂ and NF@MnO₂ at 1 mA cm⁻². d) EIS curves of NNA@MnO₂ and NF@MnO₂ (inset: magnified EIS curves at high frequency). e) Bode phase plot of NNA@MnO₂ and NF@ MnO₂. f) Cycling performance of NNA@MnO₂ at 10 mA cm⁻².



Figure 4. a) CV curves of NNA@MnO₂ of different mass loading measured at 1 mV s⁻¹. b) Gravimetric capacitance and areal capacitance of NNA@MnO₂ of different mass loading measured at 1 mV s⁻¹. c,d) CV curves of NNA@MnO₂ samples at the mass loading of 0.30 mg cm⁻² (c) and 10.81 mg cm⁻² (d).

In order to determine the contribution of MnO₂ to the electrode capacitance clearly, we conducted a CV test. As shown in Figure 4a, the CV curves within the potential window from 0 to 0.8 V were collected from NNA@MnO2 electrodes with the MnO_2 mass loading ranging from 0.3 to 16.99 mg cm⁻² (scan rate: 1 mV s⁻¹). The current response increases with the increment of the mass loading, in accordance with the improvement of the total capacitance. An EIS study on NNA@MnO2 with different mass loadings was also carried out (Figure S21, Supporting Information), where the plots featured with a vertical curve indicates a nearly ideal capacitive behavior. Besides, the corresponding time constant τ_0 also shows a similar tendency. We can conclude from the above phenomenon that the increased thickness of MnO₂ will reduce the efficiency of both ion diffusion and electron transfer. The fitting results of series resistance values are displayed (Table S5, Supporting Information). The effect of scan rate on electrochemical performance of NNA@MnO2 samples was investigated using ratedependent CV curves (Figure 4c,d). When the mass loading of MnO₂ was 0.30 mg cm⁻², the CV curves presented a nearrectangular shape, resulting from a fast and reversible ionic diffusion process of electrolyte in the nanostructured MnO₂ (Figure 4c). When the mass loading of MnO₂ increased (e.g., 10.81 mg cm⁻²), the CV curves became spindle-like, indicating lagged charge diffusion response due to the weak conductivity of MnO₂. To have a direct overview of the capacitive features of NNA@MnO2, gravimetric and areal capacitances measured at 1 mV s⁻¹ were calculated and are plotted in Figure 4b. The electrochemical performance of NNA@PPy electrodes was also studied (Figure S22, Supporting Information). Briefly, the NNA@PPy electrode exhibited gravimetric and areal

capacitances of 753.8 F g^{-1} and 376.9 mF $\rm cm^{-2}$ at a scan rate of 1 mV $\rm s^{-1},$ respectively, with a capacity retention of 95.4% after 20 000 cycles.

The enhancement of the electrochemical performance of the electrode materials can be mainly attributed to the following reasons: i) the ordered nanowire array can provide larger surface area as compared to conventional NF; ii) the superhydrophilic NNA nanostructure can provide excellent ohmic contact with both the electrode materials and substrate, which renders excellent electron transportation efficiency and electrolyte accessibility; and iii) the convex surface profile of NNA helps release the stress at the Ni/MnO₂ interface caused by repeated charge–discharge cycling.

To assess the performance characteristics of this technology at the device level, we further fabricated the NNA@MnO₂// NNA@PPy asymmetric supercapacitor (NNA-ASC) for detailed analyses (Figure 1). The typical GCD curves are plotted in Figure 5a. The NNA-ASC manifests a high areal capacitance of 135.15 mF cm⁻² at 3 A g⁻¹, and the superior electrochemical performance is among the best of recently reported advanced miniaturized supercapacitor devices (Table S7, Supporting Information). It is noteworthy that the capacitance retention was 92.7% when the current density increased to 24 A g⁻¹, and this was understandable as the NNA's charge transfer "highways" can significantly improve the rate performance.^[20] The deviation of GCD curves from the nonlinear voltage-time relationship for NNA-ASC indicates fast redox reactions in the electrodes. Additionally, all the NNA-based electrodes could be compressed down to about 20% of their original thickness by a glass slide during packaging (Figure S8, S20, and S26, Supporting Information), which could render the total thickness of



Figure 5. a) GCD curves of the NNA-ASC sample at different current densities. b) EIS plot of NNA-ASC (inset: magnified plots at the high-frequency region). c) Cycling performance of NNA-ASC at a current density of 30 A g⁻¹. d) CV profile of NNA-ASC. e) A small piece of NNA-ASC could light up an LED and drive a mini-motor propeller. f) Ragone plot of NNA-ASC compared to some most advanced energy-storage devices (by mass of the active materials).

the NNA-ASC to be about half of the height of the NNA itself. With this benefit,^[29] the NNA-ASC was both very flexible and superior in volumetric energy and power densities (Figure S25, Supporting Information), i.e., 1.23 mWh cm⁻³ and 32.16 W cm⁻³, respectively. Besides, EIS and CV tests of the compressed electrodes suggested insignificant variations in both charge-transfer efficiency and electrochemical capacity (Figure S20, Supporting Information).

The superior rate performance of the NNA-ASC can be attributed to the extremely low series resistance evidenced by EIS analysis (Figure 5b). According to the EIS analysis, the series resistance of the NNA-ASC is 3.46 Ω (including R_e 2.73 Ω and $R_{\rm ct}$ 0.73 Ω). The relatively small serial resistance in the NNA-ASC suggests that the compact electrode can ensure fast charge transfer between electrodes and electrolyte. The CV profile is plotted in Figure 5d. The maximum gravimetric energy and power densities are 48.88 W h kg⁻¹ and 1275 W kg⁻¹, respectively, which are among the best results of MnO2based symmetric and asymmetric supercapacitors and other advanced supercapacitors recently reported (Figure 5f).^[27,30-33] Additionally, the Ragone plots calculated based on total mass of the electrode are displayed in Figure S27 (Supporting Information).^[34,35] Besides, the NNA-ASC displays outstanding cycling stability with the capacitance retention of 106.6% after 20 000 cycles (Figure 5c). The outstanding energy and power features were further demonstrated by lighting a light emitting diode (LED) or driving a mini-motor propeller with one fully charged NNA-ASC (Figure 5e). Additionally, the excellent mechanical flexibility of NNA-ASC was demonstrated by measuring CV curves at different bending angles (Figure S28, Supporting Information). Thereafter, the design of hierarchical electrode with 3D structure in the present paper can excellently cater to various active materials such as transition metal oxides and conductive polymers, rendering superior electron and ion transport efficiency, short solid-state diffusion length, compressibility, and high mass loading, which are all features of the essential requirements for the flexible, miniaturized, and highperformance electronic device applications.

In summary, we have demonstrated the scalable and controllable preparation of ultralong, densely packed, and highly oriented NNA via a solution-based chemical-deposition process induced by an applied magnetic field, and systematically investigated its application as the electrode scaffold for supercapacitors. The NNA showed excellent conductivity, ultrahigh aspect ratio, and a unique vertically aligned geometry. As compared with the conventional porous electrode structures, the wellaligned, open-porous, and superhydrophilic NNA nanostructure provides numerous ion and electron transport "highways" for the active materials deposited on the NNA surface, which is especially effective in promoting the performance characteristics of the active materials. Additionally, the convexity of Ni nanowires helps to reduce stress inside the active materials during cycling. By tuning the fabrication parameters, varied active materials with adjustable electrode thickness, mass loading, and nanostructure can be obtained, which can cater to different characteristic kinetics of a given electrochemical system. Additionally, the Ni nanowires were discretely rooted on the metal foil substrate robustly, and thus the NNA-ASC could be compressed up to about fourfold thinner without degrading the electrochemical performance. We envisage this technology would arouse interests in a wide range of promising energy conversion and storage applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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