\[ \beta\text{-Ni(OH)}_2 \] Nanosheet Arrays Grown on Biomass-Derived Hollow Carbon Microtubes for High-Performance Asymmetric Supercapacitors

Qian Li, Chunxiang Lu, Dengji Xiao, Huifang Zhang, Chengmeng Chen, Lijing Xie, Yaodong Liu, Shuxia Yuan, Qingqiang Kong, Ke Zheng and Junqing Yin

The design and fabrication of biomass-based energy storage devices is becoming a new trend to reduce the depletion of non-renewable resources. Herein, \( \beta\text{-Ni(OH)}_2 \) nanosheet arrays grown on willow catkins-derived hollow carbon microtubes is prepared for the first time through a facile acid treatment and subsequent hydrothermal process. In the \( \beta\text{-Ni(OH)}_2 \@\text{acid-treated carbon microtube} \) composite, \( \beta\text{-Ni(OH)}_2 \) nanosheet arrays can be controllably grown on both internal and external surfaces of carbon microtubes, realizing effective utilization of the hollow tubular structure. In addition, carbon microtubes are not only employed as an effective support for the dispersion of \( \beta\text{-Ni(OH)}_2 \) nanosheets, but also served as a long-range conductive micro-current collector for electron transfer. Furthermore, the hollow tubular structure accompanied by the capillary effect provides fast channels for ion diffusion. As a consequence of this unique hierarchical structure, the electrode based on the \( \beta\text{-Ni(OH)}_2 \@\text{ACMT composite} \) exhibits a high specific capacitance of \( 1568 \text{ F g}^{-1} \) at 1 A g\(^{-1} \), remarkable capacitance retention of 51.0\% even at 20 A g\(^{-1} \), and excellent cycling stability of 84.3\% retention after 3000 cycles. An asymmetric supercapacitor, with \( \beta\text{-Ni(OH)}_2 \@\text{ACMT composites} \) as the positive electrode and porous carbon microtubes as the negative electrode, achieves a high energy density of 37.8 Wh kg\(^{-1} \) at 750 W kg\(^{-1} \), indicating its potential application in energy storage devices.

1. Introduction

Because of the increasing concerns on the depletion of petroleum and environmental pollutions, clean and sustainable energy technologies are drawing more and more attentions. Supercapacitors, as one of the most promising energy storage devices, have attracted great attention due to their high power density, fast charge-discharge rate and long cycle life.\(^{[1-3]} \) Supercapacitors can be divided into two categories based on charge storage mechanisms:\(^{[4]} \) 1) Electric double layer capacitors (EDLCs), generally made up of carbon-based materials, which have high power density and cycling stability but low capacitance; 2) Pseudocapacitors, generally consisting of conductive polymers and metal oxides/hydroxides, which have high specific capacitance and energy density but low stability. Among various pseudocapacitive materials, nickel hydroxide (Ni(OH))\(_2\) is considered as a promising candidate for supercapacitor owing to its high theoretical specific capacitance, well-defined redox transitions and cost efficiency.\(^{[4,5]} \) Ni(OH)\(_2\) has two polymorphs: \( \alpha\text{-Ni(OH)}_2 \) and \( \beta\text{-Ni(OH)}_2 \). Generally, \( \beta\text{-Ni(OH)}_2 \) shows better structural stability and reversibility than \( \alpha\text{-Ni(OH)}_2 \) in strong alkaline electrolyte,\(^{[6-8]} \) so it has been expected to show desirable electrochemical performances. However, the practical application of \( \beta\text{-Ni(OH)}_2 \) based electrodes is still limited by its poor dispersion\(^{[9]} \) and low electrical conductivity,\(^{[10]} \) thereby leading to compromised capacitance, poor rate capability and short cycle life.

To maximize the inherent properties of \( \beta\text{-Ni(OH)}_2 \), many carbon-based materials with large surface area and high electrical conductivity have been introduced to develop metal hydroxides/carbon composite, including graphene\(^{[5,11]} \), activated carbons\(^{[11]} \), carbon nanotubes (CNTs)\(^{[12,13]} \) and carbon fibers (CFs).\(^{[14,15]} \) Among these carbon materials, the materials with one-dimensional (1D) structure, such as CNTs and CFs, can provide long-range pathways for effective electron and ion transfer, thus endowing the whole composite with high power characteristics. However, the preparation methods of these carbon materials are complicated, costly, and environmentally harmful.\(^{[16,17]} \) Hence, it is still urgent to seek one-dimensional carbon materials with well-designed structure prepared by...
facile, inexpensive and green strategy for supercapacitor application.

Recently, the biomass material, owing to their renewability, cheapness and environmental friendliness, has become an attractive precursor to preparing carbonaceous materials. A various of biomasses, such as watermelon leaves, bamboo char, boat-fruitied sterclia seed and pomelo peel have been widely employed to fabricate carbon materials, which not only significantly reduce the cost, but also highly inherit the original extraordinary microstructures of the natural resources. Willow catkin is one kind of novel biomass precursors with 1D hollow tubular microstructure (6–10 μm in diameter, Figure S1). The long-range hollow tube of willow catkin, accompanied by its intrinsic capillarity, facilitates the transportation of moisture and nutrients. Therefore, willow catkin can be served as a bio-template to prepare hollow carbon microtube and a carbon matrix to support active nanomaterials. On the other hand, the flying willow catkins not only inevitably result in environmental pollution, but also severely affect human health, leading to runny nose, asthma, skin irritation and other complications. Hence, it is essential to develop a green and low-cost approach for the effective utilization of willow catkins.

In this work, we prepared a novel composite of β-Ni(OH)₂ nanosheet arrays grown on willow catkins-derived hollow carbon microtube (β-Ni(OH)₂@ACMT) with hierarchical structure for the first time via facile acid treatment and subsequent hydrothermal process. The hierarchical structure not only provides the external surface of carbon microtube for charge storage, but also makes the internal surface accessible, resulting in sufficient active sites for redox reactions. Carbon microtube can serve as a long-range conductive collector for electron transfer, and its hollow tubular structure accompanied by capillary effect provides fast channels for ion diffusion. Combining the high pseudocapacitance of β-Ni(OH)₂ and the high power characteristics of carbon microtube together, the as-obtained β-Ni(OH)₂@ACMT composite electrode exhibits high specific capacitance of 1568 F g⁻¹ at 1 A g⁻¹, remarkable capacitance retention of 51.0% even at 20 A g⁻¹, and excellent cycling stability of 84.3% retention after 3000 cycles. As the positive electrode, the β-Ni(OH)₂@ACMT composites were further fabricated into an asymmetric supercapacitor with porous carbon microtubes (PCMTs) as negative electrode, which achieves a high energy density of 37.8 Wh kg⁻¹ at 750 W kg⁻¹. Above all, this work provides a new structure model for biomass-derived electrode materials towards high-performance supercapacitor.

2. Results and Discussion

The preparation of the β-Ni(OH)₂@ACMT composite is shown in Figure 1. Carbon microtubes (CMTs) were synthesized by carbonization of willow catkins under Ar atmosphere at 500 °C for 4 h. The CMTs were first treated by acid treatment (denoted as ACMTs), which is a key factor for the growth of Ni(OH). The C₁s XPS spectra of the pristine CMTs and ACMTs (Figure 2) can be deconvoluted into four peaks: unmodified carbon (C–C or C=C), hydroxyl (C–O), carbyl (C=O), and carboxyl (HO–C=O) groups, respectively. After acid-treatment, the percentage of oxygen-containing functional groups as well as the [C(O)]/[C] ratio dramatically increased (Figure 2 and Table 1), indicating the high degree of surface functionalization of willow catkins.

![Figure 1. Schematic illustration of the preparation of β-Ni(OH)₂@ACMT composite.](image-url)

![Figure 2. C₁s XPS spectra of the pristine CMTs and ACMTs. The inset shows comparative photos of CMTs and ACMTs suspension in deionized water stand for 12 h.](image-url)

<table>
<thead>
<tr>
<th>Peak assignment</th>
<th>C–C or C=C [%]</th>
<th>C–O [%]</th>
<th>C=O [%]</th>
<th>HO–C=O [%]</th>
<th>[C(O)]/[C] [%]</th>
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<tr>
<td>CMT</td>
<td>70.54</td>
<td>12.31</td>
<td>8.98</td>
<td>8.17</td>
<td>29.46</td>
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<td>ACMT</td>
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<td>12.51</td>
<td>9.05</td>
<td>14.06</td>
<td>35.62</td>
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[a] Ratio of the C atoms in oxygen-containing functional groups (including C–O, C=O, and HO–C=O) to all the C atoms detected.
oxidation. The increase of carboxyl (HO–C–O) group from 8.17% to 14.06% greatly improved the wettability and hydrophilicity of carbon microtubes (inset of Figure 2), which is favorable for the adsorption of carbon microtubes towards metal cations from solution (Figure S2). Thus, more Ni$^{2+}$ ions were adsorbed on both internal and external surfaces of ACMT through the electrostatic interaction between the sufficient oxygen-containing functional groups of ACMT and Ni$^{2+}$ ions. After hydrothermal treatment at 150 °C for 6 h, the Ni(OH)$_2$@ACMT composite was obtained.

The structures and morphologies of the samples are presented in Figure 3. The ACMTs maintain the hollow tube structure with a diameter of 6–10 μm (Figure 3a and b) and a wall thickness of 200–400 nm (Figure 3b). After hydrothermal treatment, ACMTs are completely covered with β-Ni(OH)$_2$ nanosheets (Figure 3c). Figure 3d shows these β-Ni(OH)$_2$ nanosheets vertically grow on ACMT and contact with each other compactly, forming an uniform β-Ni(OH)$_2$ nanosheet array. Notably, β-Ni(OH)$_2$ nanosheets not only grow on the external surface of ACMT, but also grow on the internal surface of ACMT uniformly (Figure 3e) with a lateral size of 0.5–1 μm and thickness of 30 nm (Figure 3f), resulting in effective utilization of the hollow carbon tube and sufficient active sites for redox reaction. In contrast, without the support of ACMT, many large aggregates of Ni(OH)$_2$ microplates can be observed, as shown in Figure S3. The TEM image (Figure 3g) of β-Ni(OH)$_2$@ACMT reveals the thickness of β-Ni(OH)$_2$ arrays is about 1 μm. The TEM image of a single β-Ni(OH)$_2$ nanosheet in β-Ni(OH)$_2$@ACMT composite has also been obtained. As displayed in Figure 3h, abundant mesopores of β-Ni(OH)$_2$ nanosheet can be observed. Hydrothermal treatment promotes the crystallization of the mesoporous structure of β-Ni(OH)$_2$ nanosheet. The HRTEM image (Figure 3i) of an individual Ni(OH)$_2$ nanosheet shows two sets of clear lattice fringes with equal interplanar crystal spacing of 0.27 nm at an angle of 60°, which is corresponding to (001) plane of hexagonal β-Ni(OH)$_2$. The corresponding SAED pattern (Figure 3i) presents a perfect hexagonal spot pattern, indicating that the nanosheet has the nature of single-crystalline and is imaged along the [001] zone axis (that is, c·c-axis of β-Ni(OH)$_2$), which is consistent with the HRTEM result. Figure 3j–m are the elemental mapping images of β-Ni(OH)$_2$@ACMT. The elements of C, O and Ni achieve homogeneous distribution on the surface of the sample, which is in accord with the SEM results (Figure 3c–f).

To investigate the effect of loading mass of Ni(OH)$_2$ on the morphology of Ni(OH)$_2$@ACMT composite, TGA curves and SEM images of Ni(OH)$_2$@ACMT composites with different Ni(OH)$_2$ loading are shown in Figure S4 and Figure S5. Low Ni(OH)$_2$ content (Ni(OH)$_2$@ACMT-1, 29.6%) results in randomly growing of α-Ni(OH)$_2$ nanosheets and inadequate utilization of ACMT substrate (Figure S5a and b). High Ni(OH)$_2$ content (Ni(OH)$_2$@ACMT-3, 77.0%) leads to large lateral size of 2–4 μm and thickness of about 300 nm with many stacked β-Ni(OH)$_2$ nanosheets (Figure S5e and f), which is bad for fast electrochemical reaction. Optimized Ni(OH)$_2$ content (β-Ni(OH)$_2$@ACMT, 60.4%) can achieve a highly-dispersed and uniform growth of β-Ni(OH)$_2$ nanosheets both on the internal and external surfaces of ACMT (Figure S5c and d), which is more suitable for effective redox reactions.

To further study the growth mechanism of Ni(OH)$_2$ in β-Ni(OH)$_2$@ACMT composite and the phase transformation of Ni(OH)$_2$, the XRD patterns of β-Ni(OH)$_2$@ACMT composite prepared at different reaction time are shown in Figure 4. For ACMT, two broad peaks were detected at 22.8° and 43.2°, matching the (002) and (100) planes of graphitic carbon layer. For β-Ni(OH)$_2$@ACMT composite, when the reaction time was 1 h, a very low diffraction intensity of α-Ni(OH)$_2$ can be observed besides the feature of ACMT, which can speculate that the Ni$^{2+}$ adsorbed on the surface of ACMT tend to preferentially form α-Ni(OH)$_2$ at the initial reaction stage. After 2 h reaction time, the crystallization of α-Ni(OH)$_2$ is enhanced, as proved by the higher diffraction intensity. As the reaction proceeds to 3 h, the XRD pattern of Ni(OH)$_2$ contains both α and β phases. The peaks corresponding to β-phase are (001), (100), (101), (102), (110), and (111) planes. Only one peak indexed to α-phase is (001) plane, and interestingly, the (001) plane shifts from 11.36° to 14.02°. That is to say the interlayer space shrinks from 0.778 to 0.631 nm, indicating that the transforming trend of Ni(OH)$_2$ from α to β-phase occurred. This phenomenon can also be observed in other previous reports. With reaction time further increasing to 4 h, all the peaks can be ascribed to β-Ni(OH)$_2$, illustrating the complete transformation, in consistent with TEM results (Figure 3i). The results reveal that Ni(OH)$_2$ firstly nucleated and grew on the surface of ACMT in the form of α-phase, then α-phase gradually transformed into β-phase, and finally the β-Ni(OH)$_2$ nanosheets with better crystallization were obtained. In addition, the XRD patterns of Ni(OH)$_2$@ACMT composites with different Ni(OH)$_2$ loading are also discussed in details (Figure S6). Low Ni(OH)$_2$ content (Ni(OH)$_2$@ACMT-1) leads to Ni(OH)$_2$ in α-phase and increased Ni(OH)$_2$ content (β-Ni(OH)$_2$@ACMT and Ni(OH)$_2$@ACMT-3)
Ni(OH)₂@ACMT composite exhibits a pore size distribution higher than that of pure Ni(OH)₂ (27.3 m² g⁻¹), allowing high active specific surface area and ion transfer is also important for electrode material. The N₂ adsorption–desorption isotherms of Ni(OH)₂@ACMT and pure Ni(OH)₂ are also investigated (Figure S8). The mesopores in β-Ni(OH)₂@ACMT composite are favorable for the transport of ions and electrons.\(^{[26,31]}\)

The electrochemical performances of the samples were evaluated in a three-electrode system. Figure 6a compares the cyclic voltammetry (CV) curves of β-Ni(OH)₂@ACMT and pure Ni(OH)₂ electrodes at 20 mVs⁻¹. Both of the CV curves show a pair of well-defined redox peaks, illustrating that the electrochemical capacitance is dominated by the reversible faradic redox reactions, as shown in Equation (1).\(^{[33,34]}\)

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-
\]

Notably, it can be noted that β-Ni(OH)₂@ACMT electrode exhibits a larger CV curve area than those of pure Ni(OH)₂, implying a significantly enhanced specific capacitance. Moreover, the potential difference between cathodic peak and anodic peak of β-Ni(OH)₂@ACMT electrode is shorter than that of pure Ni(OH)₂ electrode, indicating that β-Ni(OH)₂@ACMT electrode has an improved electrochemical reversibility.\(^{[33,34]}\)

The representative CV curves of β-Ni(OH)₂@ACMT electrode at different scan rates are shown in Figure 6b. With scan rates increasing, the positions of redox peaks shift very slightly, and the shape achieves well-maintained, indicating the high rate performance. This can be attributed to the long-range conductive ACMT and its intimate contact with β-Ni(OH)₂ nanosheets. Galvanostatic charge-discharge (GCD) curves of β-Ni(OH)₂@ACMT electrode at different current densities are shown in Figure 6c. The nonlinear GCD curves reveal the typical pseudocapacitance behavior of β-Ni(OH)₂@ACMT electrode, which is in consistent with the CV results. In addition, the GCD curves present a relatively symmetric shape, implying the reversibility of the redox reactions. The specific capacitance of β-Ni(OH)₂@ACMT electrode achieves 1568 F g⁻¹ at 1 A g⁻¹ (Figure 6d), indicating that β-Ni(OH)₂@ACMT electrode has a good rate capability. In addition, the specific capacitance of Ni(OH)₂@ACMT composites with different mass ratio are also investigated (Figure S8). The β-Ni(OH)₂@ACMT sample is deduced to exhibit the highest capacitance, which can be ascribed to the appropriate growth of Ni(OH)₂ nanosheet arrays on the surface of carbon microtubes to provide abundant electrode/electrolyte interface for redox reaction. Furthermore, the capacitance retention of β-Ni(OH)₂@ACMT electrode is significantly higher than that of pure Ni(OH)₂ (11.8% of capacitive retention), suggesting that it is an efficient way to improve the capacitance of pseudocapacitive materials by fixing them on the surface of one

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**Figure 4.** XRD patterns of ACMT and β-Ni(OH)₂@ACMT composite prepared at different reaction times.

**Figure 5.** a) N₂ adsorption–desorption isotherms and b) pore-size distributions of β-Ni(OH)₂@ACMT composite and pure Ni(OH)₂.
To further analyze the electrochemical properties of β-Ni(OH)2@ACMT and pure Ni(OH)2 electrodes, electrochemical impedance spectroscopy (EIS) was tested in the frequency range of 100 kHz to 0.01 Hz with an amplitude of 5 mV (Figure 6e). Generally, the Nyquist plots are consisted of a semicircle in high-frequency region and a sloping line in low-frequency region.\[35\] In high-frequency region, the intersection of the plot corresponds to the equivalent series resistance ($R_s$), including the interface contact resistance, the inherent resistance of the electrodes and the ionic resistance of electrolyte. The diameter of the semicircle represents the charge-transfer resistance ($R_{ct}$) for redox reactions between electrodes and electrolyte interface. The inset of Figure 6e shows the corresponding equivalent circuit model, where $R_s$, $C_{dl}$, $R_{ct}$, $W$ and $C_F$ represents the equivalent series resistance, the double-layer capacitor, the charge-transfer resistance, the Warburg impedance and the pseudocapacitive element, respectively. Based on the equivalent electrical circuit model, the $R_s$ of β-Ni(OH)2@ACMT electrode and pure Ni(OH)2 electrode is 0.55 W and 0.54 W, respectively. In addition, no apparent semicircle can be observed for β-Ni(OH)2@ACMT electrode compared with that of pure Ni(OH)2 electrode. The $R_{ct}$ of β-Ni(OH)2@ACMT electrode and pure Ni(OH)2 electrode is 0.06 W and 0.62 W, respectively, indicating...
that $\beta$-Ni(OH)$_2$@ACMT composite possesses higher conductivity than pure Ni(OH)$_2$. Furthermore, the slope of the plot in low-frequency region represents the diffusive resistance in accordance with the ion diffusion process.\cite{28} Obviously, $\beta$-Ni(OH)$_2$@ACMT electrode presents a steeper slope than that of pure Ni(OH)$_2$ electrode, implying that $\beta$-Ni(OH)$_2$@ACMT electrode has a lower Warburg impedance and faster ion diffusion between electrolyte and electrode surface. The cycling performance of $\beta$-Ni(OH)$_2$@ACMT electrode was evaluated at 5 A g$^{-1}$ (Figure 6f). Impressively, the specific capacitance of the electrode increases in the first 200 cycles, which is likely ascribed to the activation process.\cite{36,37} It generally takes time for the electrolyte ions to gradually penetrate into the interior of $\beta$-Ni(OH)$_2$@ACMT composite. This phenomenon can be also observed in other previous reports.\cite{36,37} As a result, the specific capacitance of $\beta$-Ni(OH)$_2$@ACMT electrode increases in the earlier stage of the cycles. Afterwards, the specific capacitance decays slightly to 1012 F g$^{-1}$ after 3000 cycles with a high capacitance retention of 84.3%, showing an obviously improved cycling stability than that of pure Ni(OH)$_2$ (61.7%, Figure S9). The SEM and TEM images of $\beta$-Ni(OH)$_2$@ACMT composite after cycling performance are shown in Figure 7. After cycling performance, several $\beta$-Ni(OH)$_2$ nanosheets suffer some collapse, and the corresponding agglomerates can be observed (Figure 7a and b). Analysis of the TEM image in Figure 7d also shows that the $\beta$-Ni(OH)$_2$ nanosheets have agglomeration to some extent. But more importantly, although part of $\beta$-Ni(OH)$_2$ nanosheets collapse slightly, the whole structure of the $\beta$-Ni(OH)$_2$@ACMT composite maintains well (Figure 7a and Figure 7c), without serious damage, indicating a robust structure of $\beta$-Ni(OH)$_2$@ACMT composite to endure repeated cycling processes. The last five GCD curves of $\beta$-Ni(OH)$_2$@ACMT electrode (Inset, Figure 6f) remain similar shapes to those of the first five cycles, implying its excellent reversibility. The excellent electrochemical performance of $\beta$-Ni(OH)$_2$@ACMT composite can be mainly attributed to five reasons (Figure 6g): 1) The uniform distribution of ultrathin $\beta$-Ni(OH)$_2$ nanosheets on both internal and external surfaces of hollow tubular ACMT can obviously enhance their specific surface area and enable more electroactive sites for efficient redox reactions. 2) Each $\beta$-Ni(OH)$_2$ nanosheet is consist of many atomic layers. The redox reaction between two atomic layers leads to the reversible transformation between $\beta$-Ni(OH)$_2$ (46 Å) and $\beta$-NiOOH (48 Å), further providing desirable pseudocapacitance. 3) The electrons generated from redox reactions can transfer between different $\beta$-Ni(OH)$_2$ nanosheets because of the close contact between them, and then pass on to conductive ACMT due to the compact combination between ACMT and $\beta$-Ni(OH)$_2$ nanosheets. 4) With tens of micrometers in axial, the ACMT can serve as a long-range conductive micro-current collector. Therefore, electrons can transfer through the whole tube rapidly and directly. 5) The hollow tubular structure of the composite accompanied by capillary effect and hydrophilicity provides fast channels for electrolyte ion diffusion.

To further understand the practicality of the $\beta$-Ni(OH)$_2$@ACMT for energy storage, an asymmetric supercapacitor (ASC) was assembled by using $\beta$-Ni(OH)$_2$@ACMT composites as positive electrode and PCMTs as negative electrode (denoted as $\beta$-Ni(OH)$_2$@ACMT//PCMT), as shown in Figure 8a. The morphologies and electrochemical properties of PCMTs are shown in Figure S10 and Figure S11, respectively. The mass ratio of $\beta$-Ni(OH)$_2$@ACMT (3 mg) and PCMT (9.3 mg) was calculated to be 1:3.1, which was based on the charge balance Equation (3) and their specific capacitances (253 V s$^{-1}$ 1568 F g$^{-1}$). The voltage window of $\beta$-Ni(OH)$_2$@ACMT//PCMT ASC was enlarged to 1.5 V, according to the respective voltage window of two electrodes. Figure 8b presents the CV curves of ASC, and the shape of the curves maintains well even at 50 mV s$^{-1}$, implying its fast charge-discharge characteristics. Moreover, the GCD curves at different current densities (Figure 8c) are almost symmetric, suggesting a good reversibility. The specific capacitance of the ASC is calculated to be 121 F g$^{-1}$ at 1 A g$^{-1}$, and still remains 43.8% capacitance retention even at 20 A g$^{-1}$ (Figure 8d). This good rate capability is related with the hierarchical structure of both $\beta$-Ni(OH)$_2$@ACMT composite and PCMT. The cycling performance of $\beta$-Ni(OH)$_2$@ACMT//PCMT ASC was evaluated at 5 A g$^{-1}$ for 3000 cycles (Figure 8e). The specific capacitance increases in the first 450 cycles, which may arise from the gradually penetration of electrolyte into the interior of electrode materials.\cite{26} After the whole device is fully activated, however, the specific capacitance decays slightly in the subsequent cycles, which is not only ascribed to the degradation of both of positive and negative electrode materials, but also is related to other factors such as the depletion of electrolyte and the gradually unbalanced matching between positive and negative electrodes.\cite{45} Even so, the capacitance retention still remains 80.8% after 3000 cycles, implying an excellent cycling performance. The GCD curves of 3000th cycle maintains well compared with the 1st cycle, suggesting high reversibility of the ASC. The Ragone plots (Figure 8f) show that the $\beta$-Ni(OH)$_2$@ACMT//PCMT ASC achieves a high energy density of 37.8 Wh kg$^{-1}$ at 750 W kg$^{-1}$, and still remains 16.6 Wh kg$^{-1}$ at 15 kW kg$^{-1}$. Moreover, the results are better than or at least comparable to some other Ni(OH)$_2$-based ASCs,\cite{19,12,40–44} as shown in Figure 8f. Furthermore, a LED was lighted up by two ASCs assembled in series (inset of Figure 8f).
57 further implying the practical application of the ASC in energy storage.

3. Conclusions

In summary, β-Ni(OH)₂ nanosheets were anchored on willow catkins-derived hollow carbon microtube through facile acid treatment and subsequent hydrothermal process, and a novel hierarchical structure of β-Ni(OH)₂@acid-treated carbon microtube (β-Ni(OH)₂@ACMT) composite was obtained. The hierarchical structure not only provides the external surface of hollow tube for charge storage, but also makes the internal surface accessible. The morphology and crystal structure of the Ni(OH)₂@ACMT composite could be controlled by regulating the precursor dosages of Ni(NO₃)₂ · 6H₂O/NH₄F/urea. The corresponding products were denoted as Ni(OH)₂@ACMT-1, Ni(OH)₂@ACMT-2 and Ni(OH)₂@ACMT-3, respectively. For comparison, pure Ni(OH)₂ was prepared by the same process.

**Experimental Section**

**Preparation of the β-Ni(OH)₂@ACMT Composite**

Carbon microtubes (CMTs) were fabricated by carbonization of willow catkins under Ar atmosphere at 500 °C for 4 h. Then, the CMTs (0.5 g) were refluxed with a mixture of HNO₃ (67%, 150 mL) and deionized water (150 mL) at 120 °C for 5 h. After cooling, the products were filtered, washed with deionized water three times, and dried by freeze-drying. The acid treated CMTs were donated as ACMTs. The ACMTs (80 mg) were dispersed in 80 mL deionized water by stirring for 30 min. Then, Ni(NO₃)₂ · 6H₂O (1.4 mmol), NH₄F (7 mmol) and urea (7 mmol) were added into the above dispersion. After stirring for 30 min, the mixed dispersion was transferred into an autoclave at 150 °C for 6 h. Finally, the products (denoted as β-Ni(OH)₂@ACMT) were washed with deionized water several times, and dried by freeze-drying. In order to investigate the effect of the loading mass of Ni(OH)₂ on the morphology, crystal structure and electrochemical performance of Ni(OH)₂@ACMT composite, a series of Ni(OH)₂@ACMT composites were prepared by regulating the precursor dosages of Ni(NO₃)₂ · 6H₂O (i.e., 0.4 mmol, 1.4 mmol and 3.4 mmol) at a fixed molar ratio of 1/2/5 for Ni(OH)₂, Ni(OH)₂/NH₄F/urea. The corresponding products were denoted as Ni(OH)₂@ACMT-1, β-Ni(OH)₂@ACMT and Ni(OH)₂@ACMT-3, respectively. For comparison, pure Ni(OH)₂ was prepared by the same process.
Characterization

The structures and morphologies of the samples were evaluated by SEM (JSM-7001F), TEM (JEM-2010) and XRD (Bruker D8 Advance, Cu Kα, radiation, λ = 0.154060 nm). The surface chemistry of carbon microtubes was observed by XPS (ESCALAB 250XI) with Al Kα radiation (1486.6 eV). Nitrogen adsorption-desorption analysis was evaluated on Micromeritics ASAP 2020 at 77 K. The specific surface area was conducted by the Brunauer-Emmett-Teller (BET) analysis. Pore size distribution was analyzed from desorption branch by Barrett-Joyner-Halenda (BJH) model. Thermogravimetric analysis (NETSCH STA409PC) was conducted under air at 10 °C min⁻¹.

Electrochemical Tests

The electrochemical properties were evaluated in a three-electrode system by an electrochemical workstation (CHI 660E, Shanghai) with Hg/HgO as reference electrode and platinum foil as counter electrode in 6 M KOH. The working electrode was prepared by blending the prepared products (85%), carbon black (10%) and polyfluorotetraethylene (5%) together into a slurry, followed by pressing on nickel foams (1.0 /C148 1.0 cm²) and drying at 60 °C for 24 h. The thickness of the electrode was about 55 μm (Figure S12). The mass loading of the active materials in an electrode was about 9.3 mg (i.e., 3 mg cm⁻²). Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were conducted between of 0–0.5 V. Electrochemical impedance spectroscopy (EIS) measurement was tested in the frequency range of 100 kHz to 0.01 Hz with an amplitude of 5 mV. The specific capacitance (C, F g⁻¹) is calculated from charge-discharge curves by using Equation (2):[46,47]

\[
C = \frac{l \times \Delta t}{\Delta V \times m}
\]

where \(l\) (A), \(\Delta t\) (s), \(m\) (g) and \(\Delta V\) (V) represent the discharge current, discharge time, mass of electrode materials and voltage window, respectively.

The electrochemical measurements of asymmetric supercapacitor were evaluated in a two-electrode cell. The asymmetric supercapacitor was assembled by using \(\beta\)-Ni(OH)₂@ACMT composites as positive electrode and PCMTs as negative electrode, with a piece of polypropylene membrane as separator and 6 M KOH as electrolyte. The PCMTs were prepared from willow catkins via a carbonization process on a carbon membrane as separator and 6 M KOH as electrolyte. The optimal mass ratio of \(\beta\)-Ni(OH)₂@ACMT and PCMT was 1 : 3.1 based on the charge balance equation. The mass loading of the positive electrode and negative electrode was about 55 μm (Figure S12) and 190 μm (Figure S13), respectively. The energy density (\(E\), Wh kg⁻¹) and corresponding power density (\(P\), W kg⁻¹) are calculated by using Equations (4) and (5):[48]

\[
E = \frac{1}{2} CV^2
\]

\[
P = \frac{E}{\Delta t}
\]

where \(C\) (F g⁻¹), \(V\) (V), \(\Delta t\) (s) represent the specific capacitance, voltage window and discharge time, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

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