Scalable, Binderless, and Carbonless Hierarchical Ni Nanodendrite Foam Decorated with Hydrous Ruthenium Dioxide for 1.6 V Symmetric Supercapacitors

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Herein, Ni nanodendrite (ND) with diameter Φ=30–100 nm directly synthesized on Ni foam is utilized as an effective support for hydrous RuO$_2$ in symmetric supercapacitors operated at 1.6 V. Highest specific capacitance 678.57 F g$^{-1}$ can be achieved with energy density 60.32 Wh kg$^{-1}$. Even at large current density 100 A g$^{-1}$, high energy density 19.73 Wh kg$^{-1}$ can still be maintained with power density 40 kW kg$^{-1}$ owing to the pristine metal nanostructure without any carbon additive and resistive binder. Long lifespan is shown with marginal performance improvement (≈4%) over 10 000 cycles. More importantly, the template-less and self-assembled Ni ND synthesis requires only low temperature and eco-friendly chemicals, and can be simply dip-coated with RuO$_2$ nanoparticles. All of these render the RuO$_2$-Ni ND foam readily adapted into mass manufacturing without efforts.

1. Introduction

In the new millennium, oil crisis and acute climate change are relentlessly challenging modern society. To reduce the dependence on fossil fuels and diminish greenhouse gas emission, it is indispensable to future human civilization to deliver energy in efficient ways and harness energy from renewable sources. However, high power requirement is often demanded due to the intermittent nature of these sources, such as unstable tidal wind flow, and in regenerative recharge from braking in electric vehicles.[1] In this case, supercapacitors with higher power density than Li-ion batteries, and higher energy density than traditional capacitors will play important roles in these fields. Nonetheless, electric double-layer capacitors (EDLCs) storing energy by electrostatic charges still fail to meet the requirement because of its lower energy density.[2–4] Pseudocapacitors take advantage of fast and reversible surface redox reactions to provide 10–100 times higher energy density than EDLCs.[2] Traditional pseudocapacitor materials include conducting polymers, e.g., polyaniline (PANI),[5] polypyrrole (PPy),[6,7] and polypthiophene (PTh),[8] and transition metal oxides, such as MnO$_2$,[9,10] TiO$_2$,[11] MoO$_3$,[12] NiO,[13] Ni(OH)$_2$,[14] and RuO$_2$.[15–17] Although conducting polymer is relatively cheap, it still suffers from strict operating potential window, mechanical degradation, and short cycle life.[2] Among metal oxides, RuO$_2$, especially hydrous and amorphous RuO$_2$ exhibits superior performance resulting from its high theoretical specific capacitance (1450 F g$^{-1}$ of RuO$_2$ and 1360 F g$^{-1}$ of RuO$_2$·0.5H$_2$O over 1 V window), metallic electrical conductivity, and fast proton transport through the structural water.[1] Nevertheless, scarcity and high price of ruthenium prevent it from large scale production. Efforts have been made to minimize RuO$_2$ loading by anchoring it onto nanostructures.[17,18] Nano-porous gold electroplated with RuO$_2$ demonstrates specific capacitances (1150-1450 F g$^{-1}$) very close to theoretical value.[17] However, extremely low RuO$_2$ loading (2 to 16 µg cm$^{-2}$) and expensive gold substrate prohibit it from practical utilization. Hydroxyl RuO$_2$ anchored on graphene sheet composite (ROGSC) shows stable specific capacitance (300-570 F g$^{-1}$) for 1000 cycles.[18] Nonetheless, relative low Ru content (38.3 wt%) on ROGSC, the necessity of conductive carbon black and polytetrafluoroethylene (PTFE) binder further reduces active material loading. RuO$_2$ nanoparticles in tetragonal phase embedded in electrosynp carbon nanofibers show ≈200 F g$^{-1}$ for 3000 cycles.[19] However, RuO$_2$ nanoparticles embedded inside carbon nanofibers are inactive for surface redox reaction, and the crystalline nature further decreases its specific capacitance. Graphene and carbon nanotube (CNT) hybrid foam is synthesized as support for hydrous RuO$_2$ with specific capacitance of ≈220–500 F g$^{-1}$ and is stable over 8100 cycles.[13] Nevertheless, expensive manufacturing processes, including high vacuum e-beam evaporated Ni catalysts and high temperature graphene/CNT growth, render this support impractical for...
large scale production. Accordingly, cheap while effective RuO₂ nanostructural supports are still necessary.

Nickel is widely utilized in electrochemical devices as a result of its chemical stability, low price, and high availability. Recently, commercially available Ni nanofoam consisting of interconnected Ni nanowires is decorated with SnO₂ by atomic layer deposition. High capacity, high rate capability and stability for Li-ion anode can be achieved with this structure. Ni nanofoam with various diameters (100–1000 nm) can be synthesized by refluxing glycerol and Ni acetate (Ni(Ac)₂).[21,22] Ni can be further etched by oxalic acid into Ni oxalate nanowires and nanosheets to increase surface area,[23] which can be further reduced back to Ni metal under inert or reducing atmosphere.[24,25] In this work, Ni nanodendrite (ND, dia. =30–100 nm) attached on Ni nanowire (=300 nm in dia.) backbone is synthesized directly on Ni foam as a novel support for hydrous RuO₂ nanoparticles in symmetric supercapacitors. Ni nanoparticles are grown on HCl-treated Ni foam with Ni(Ac)₂ and glycerol at 370 °C. Ni nanowires are transformed into leaf-like Ni oxalate nanostructures by oxalic acid treatment at 120 °C. Ni oxalate nanoleaves are further reduced back to Ni ND on Ni foam (NDF) by H₂ at 350 °C. Hydrous RuO₂ nanoparticles are dip-coated onto NDF and annealed at 150 °C under vacuum without any binder and conductive additive. Highest specific capacitance (678.57 F g⁻¹) can be achieved at 0.5 A g⁻¹, with energy density 60.32 Wh kg⁻¹. Even at large current density 100 A g⁻¹, specific capacitance can still be 221.95 F g⁻¹ with high energy density 19.73 Wh kg⁻¹ and power density 40 kW kg⁻¹. The entire NDF metal support without any conductive additive and binder renders very low equivalent series resistance (ESR) ≈0.5 Ω, leading to low resistive loss and good power performance. More importantly, Ni NDF requires only low temperature production, environmentally benign chemicals, no templates for nanostructure growth, and simple dip-coating process, which can be adapted into large scale production without efforts.

2. Results and Discussion

 Hierarchical nanostructure of NDF can provide large surface area, short proton conduction pathways, and electrical conductive support for RuO₂ deposition. Schematic of synthesis and scanning electron microscopic (SEM) images of NDF are shown in Figure 1. To synthesize NDF, HCl-treated Ni foam is heated up to 370 °C with 0.08 M Ni(Ac)₂/glycerol solution (Figure 1a). Ni nanoparticles formed by reduction of Ni²⁺ ions with glycerol[21] nucleate into larger polyhedral nanoparticles, and grow into nanowires (~200–700 nm in diameter) along the magnetic field provided by the magnetic stir rotor inside the hotplate (Figure 1b). Magnetic alignment of Ni nanoparticles growing into Ni nanowires has been demonstrated in 3D nonwoven clothes,[26] which proves the feasibility of manufacturing ferromagnetic materials into self-assembled nanowires without templates. X-ray diffraction (XRD) pattern of Ni nanowires demonstrates peaks at 45.1°, 52.5° and 76.9°, which are characteristic of cubic Ni metal (ref. code: 01-070-0989, Figure 2a). Leaf-like Ni oxalate nanostructure can be obtained by etching Ni nanowires in 0.3 M oxalic acid/ethanol solution at 120 °C (Figure 1c), which can further increase surface area of the nanowires. XRD peaks at 18.9°, 23.0°, 30.4°, 35.8°, and 41.2° indicate the existence of Ni oxalate (NiC₂O₄·2H₂O, ref. code 00-014-0742). Ni oxalate can be reduced back into Ni ND by H₂ at 350°C (Figure 1d) with diameters ≈30–100 nm, which shows only Ni metal crystalline phases without presence of Ni oxalate (Figure 2a). Hydrous RuO₂ prepared by mixing RuCl₃ with NaOH is dipped onto NDF, and the whole electrode is annealed at 150 °C under vacuum (Figure 1e). Loading of RuO₂ is measured as the weight difference of NDF before and after RuO₂ coating. RuO₂ nanoflakes can be uniformly suspended on these dendritic struts, which provides intimate contact and open space for fast electrical and ionic conduction, respectively. Energy dispersive X-ray spectroscopic (EDX) analysis and element mapping (Figure S1, Supporting Information) show uniform distribution of RuO₂ on NDF with a trace amount of Na ions from the reaction by-products. XRD pattern of the RuO₂-coated NDF shows only Ni metal phase (Figure 2a), which indicates the hydrous RuO₂ is amorphous. High resolution transmission electron microscopic (HRTEM) image (Figure 2b) of the hydrous RuO₂ shows that RuO₂ nanoparticle diameters range from 2–3 nm. Most of the nanoparticles do not demonstrate lattice fringes, and very weak diffraction rings of selected area electron diffraction pattern further confirm the amorphous nature of the hydrous RuO₂.

Hydrous nature of RuO₂ synthesized by sol–gel process and low temperature annealing is further elucidated by X-ray photoelectron spectroscopy (XPS). O 1s peak (Figure 3a) for Ru-O-Ru from RuO₂ is at 529.1 eV,[27] while the co-adsorbed H₂O–OH layer with OH and H₂O hydrogen bonded to each other results in peaks at 530.4 and 531.6 eV from OH (HO–H₂O) and water (H₂O–OH), respectively.[28] Ru 3p (Figure 3b) is deconvoluted into RuO₂ (462.0 eV)[29] and RuOH (464.2 eV)[15] signals exhibiting an intensity ratio of 1 : 0.9. Ru 3d (Figure 3c) shows seven constituents including Ru 3d₁₂ of RuO₂ at 286.0 eV[29] RuOH at 282.6 eV[15] and at 281.4 eV from final-state screening effect (FS).[30] Binding energy is calibrated using C 1s peak at 285.0 eV from sample support, and the rest peaks are responsible for Ru 3d₁₂. Survey spectrum is shown in Figure S2 in the Supporting Information.

Electrochemical behaviors of the two-electrode symmetric supercapacitors consisting of hydrous RuO₂ on NDF with aqueous electrolyte (2M Li₂SO₄) and polymer separator (Celgard 3501) are demonstrated in Figure 4. Cyclic voltammograms (CVs) of the electrodes with RuO₂ loading 0.6 mg cm⁻² are shown in Figure 4a with scan rate from 10 to 200 mV s⁻¹ between 0 and 1.6 V. The rectangular shape of the CV curves without obvious redox peaks indicates ideal capacitive behaviors even at high scan rate 200 mV s⁻¹, which shows superior rate capability of the RuO₂-NDF supercapacitors. The extended potential window to 1.6 V is higher than most aqueous electrolyte supercapacitors (~1.0 V). This can be attributed to the utilization of neutral Li₂SO₄ aqueous electrolyte, which provides strong hydration energy of lithium cations and sulfate anions with water molecules leading to water decomposition potential higher than 1.23 V.[31] In addition, RuO₂ has been shown to prohibit water decomposition in neutral Na₂SO₄ aqueous electrolyte, resulting in high overpotentials for both hydrogen and oxygen evolution reactions.[32] Without RuO₂ coating, water is decomposed vigorously at 1.5 V with Ni NDF only (Figure S3,
Supporting Information). Accordingly, RuO$_2$-NDF in aqueous Li$_2$SO$_4$ electrolyte can be operated in a wide potential window, which is beneficial to reach high specific capacitance, energy, and power density. Galvanostatic charge/discharge curves of 0.6 mg cm$^{-2}$ RuO$_2$ with various current density demonstrate nearly linear and symmetric zigzag lines (Figure 4b), which indicate excellent capacitive behavior of the RuO$_2$-NDF supercapacitor. Specific capacitance

Figure 1. a) Schematic of the synthesis of Ni nanodendrite foam (NDF). SEM images of b) Ni nanowires, c) leaf-like Ni oxalate nanowires, d) Ni nanodendrites, and e) RuO$_2$-coated NDF.

Figure 2. a) XRD patterns of Ni nanowires (Ni NW), leaf-like Ni oxalate nanostructure on Ni nanowire (Ni Oxalate), Ni nanodendrite (Ni ND), and RuO$_2$-coated Ni ND (RND). b) HRTEM image of hydrous RuO$_2$ with the inset of its selected area electron diffraction pattern. Red circles indicate the lattice fringe structures of locally crystalline RuO$_2$ nanoparticles.
can provide fast electronic conduction between active material and current collector, and the open structure facilitates ionic transport between RuO$_2$ and the electrolyte. Specific capacitance of single electrode ($C_s$) is calculated by $C_s = \frac{i \Delta V}{m \Delta t}$, where $i$, $m$, $\Delta V$, and $\Delta t$ are current, mass of RuO$_2$ of one electrode, potential window, and discharge time, respectively. Current density is based on RuO$_2$ weight of one electrode. Contribution of specific capacitance from Ni ND can be considered negligible (≈3.9 F g$^{-1}$) since it contributes to only 4.8% and 2.4% for 0.3 and 0.6 mg cm$^{-2}$ RuO$_2$, respectively (Figure S4, Supporting Information). Therefore, it is reasonable to consider RuO$_2$ as the only active material. Specific capacitance increases as RuO$_2$ loading decreases from 0.9 to 0.3 mg cm$^{-2}$ because less agglomeration of RuO$_2$ nanoflakes renders more surface area of active material contributing to the pseudocapacitance (Figure S5, Supporting Information). Comparing to the specific capacitances of 0.3 mg cm$^{-2}$, similar values (2.2%–9.9% drop) are obtained for 0.6 mg cm$^{-2}$, while 23%–44% drop of capacitance is observed when it is increased to 0.9 mg cm$^{-2}$, which implies that around 0.5 mg cm$^{-2}$ might be the optimal loading for the Ni NDF.

Stability examination is performed on RuO$_2$-NDF of active material 0.3–0.9 mg cm$^{-2}$ with 10 000 charge–discharge cycles at 20 A g$^{-1}$ (Figure 4d) since long cycle life is expected for supercapacitors in practical application. After 10 000 cycles, the retention diminishes drastically to ≈40% for 0.3 mg cm$^{-2}$, while for 0.6 and 0.9 mg cm$^{-2}$ the values rise to ≈104% and 126%, respectively. It is suggested that 0.3 mg cm$^{-2}$ of RuO$_2$ is insufficient to cover the whole surface of Ni NDF (Figure S5f–f, Supporting Information), which might lead to water decomposition and O$_2$/H$_2$ gas evolution at high potential, resulting in local pH variation[33,35] and dissolution of Ni substrates,[36,37] detachment of weakly-bonded RuO$_2$ from Ni ND and consequently faded capacitance after long cycle. For 0.6 mg cm$^{-2}$, capacitance decline to ≈88% after 3000 cycles, but gradually rise to 104% after 10 000 cycles. This might result from minute O$_2$/H$_2$ evolution and Ni dissolution of uncovered Ni ND surface (Figure S5c,g, Supporting Information) inducing small amount of unstable RuO$_2$ removal in the beginning, but reduced agglomeration of RuO$_2$ nanoflakes gradually improve the capacitance. For 0.9 mg cm$^{-2}$, the surface is well covered with relatively thick RuO$_2$ layer (Figure S5h, Supporting Information), and more and more active surface is exposed to electrolyte during the cycling process. Accordingly, 0.6 mg cm$^{-2}$ might be the appropriate loading amount on the Ni NDF considering the cycling stability. High Coulombic efficiencies, defined as the percentage of discharge time over charge time,[38] ranging from 97% to 101% are achieved on all loading of RuO$_2$, which indicates they are highly efficient during charge and discharge process.

Electrochemical impedance spectroscopy (EIS) is used to discover additional information regarding the RuO$_2$-NDF supercapacitor of 0.6 mg cm$^{-2}$ RuO$_2$ (Figure 5) with complex impedance plots before and after 10 000 cycles. The equivalent circuit model and fitting parameters are shown in Figure 5a and Table 1, respectively. Equivalent series resistance (ESR) quantifies the resistances of electrolyte, current collectors, and electrode materials.[39,40] ESR diminution from 0.665 to 0.515 Ω (Table 1) after cycling might result from gradual activation of agglomerated materials, and the low ESR values indicate superior power capability. Charge transfer resistance ($R_{CT}$) is related

![Figure 3](image-url)
to the overpotential at the electrode–electrolyte interface during both cathodic and anodic electron transfer. \[41\] \(R_{\text{CT}}\) holds steady after cycling, which provides evidence for excellent stability of the electrode. Leakage resistance \(R_L\) represents irreversible capacity loss. \(R_L\) before and after cycling are still significantly high (300 and 120 \(\Omega\), respectively), indicating that current drawn to irreversible processes is negligible. Constant phase elements (CPEs) have been used to model distributed nature of capacitance in a spatially nonuniform electrochemical system. \[42\] CPE \(\text{DL}\) and CPE \(\text{P}\) are the nonuniform capacitances due to double layer formation \[43\] and pseudocapacitive RuO\(_2\) species, \[15\] respectively. CPE \(\text{P}\) decrease induced by degradation of active materials is compensated by CPE \(\text{DL}\) improvement as a result of enlarged surface area due to reduced aggregation of RuO\(_2\) nanoflakes, \[15\] which results in \(\approx 4\%\) enhancement (Figure 4d) in total capacitance after 10 000 cycles. A Warburg element \(W_0\) is utilized to model electrolyte diffusion within the porous-like electrode. Short Warburg region in the intermediate frequency range (Figure 5b,c) and insensitivity of Warburg parameters before and after cycling (Table 1) indicate no vigorous variation in ion diffusion path lengths of the electrodes is observed. \[15,44\]

Stability of the RuO\(_2\)-coated Ni NDF electrodes is further discussed by comparing the EIS spectrum (Figure S6, Supporting Information) and charge/discharge curves before and after 10 000 cycles (Figure S7, Supporting Information). Before long cycles, the EIS Nyquist plots of the three different loadings in the low frequency region show linear and vertical-like characteristics indicating ideal capacitive behaviors. \[44,45\] After 10 000 cycles, these characteristics are essentially remained with some deviations from ideality resulting from frequency dispersion of wider pore size distribution of the porous electrodes after long cycles. \[15,46\] ESR of the three different RuO\(_2\) loadings exhibit low resistance changes (0.3 mg cm\(^{-2}\): 0.689–0.711 \(\Omega\); 0.6 mg cm\(^{-2}\): 0.665–0.515 \(\Omega\); 0.9 mg cm\(^{-2}\): 0.567–0.613 \(\Omega\)). The stable ESR values indicate no severe modifications of the structure of current collector, the composition of electrolyte and electrode materials since ESR accounts for the resistances of electrolyte, current collector, and electrode materials. \[39,40\] These evidences demonstrate that serious water decomposition and Ni ND dissolution resulting in enormous electrolyte composition modification, electrode material corrosion, and structural demolition do not occur in the RuO\(_2\)-NDF electrode. Capacitive behaviors of the three RuO\(_2\) loadings before and after 10 000 cycles are manifested by the symmetric charge/discharge curves (Figure S7, Supporting Information), which show no plateaus at high potentials, indicating water decomposition or Ni dissolution are not the dominant reactions regardless of the capacitance changes after 10 000 cycles. Average Coulombic efficiency (Figure 4d) of 0.3, 0.6, and 0.9 mg cm\(^{-2}\) are 99.26%, 99.72%, and 99.86%, respectively, which show almost all charges supplied during recharge steps can be delivered back during the discharge steps. These again demonstrate the irreversible reactions, such as gas evolution \[47\] or Ni dissolution, resulting in low Coulombic efficiency are not the dominant reactions. The slightly lower Coulombic efficiency of 0.3 mg cm\(^{-2}\) corresponds to minute gas evolution or Ni dissolution, leading to loss of active materials. 

Figure 4. Electrochemical measurement of two-electrode symmetric RuO\(_2\)-NDF supercapacitors. a) CV curves with scan rate 10, 20, 50, 100, and 200 mV s\(^{-1}\), and b) galvanostatic charge/discharge curves with 0.5, 1, and 2 A g\(^{-1}\) of 0.6 mg cm\(^{-2}\) RuO\(_2\) loading. c) Specific capacitance (F g\(^{-1}\)) variations with respect to various current density and RuO\(_2\) loading. d) Capacitance retention and Coulombic efficiency relationship with various RuO\(_2\) loading and cycle number.
and capacity fading. Stabilities of Ni current collectors operated in aqueous sulfate electrolytes and high potentials have been shown in several literatures.\(^{[47-49]}\) In 0.5 M \(\text{Na}_2\text{SO}_4\) aqueous solution, Ni mesh is stable in −1.0 to 1.2 V versus saturated calomel electrode, and 10 000 cycles with slight capacitance loss (<3%) is achieved using asymmetric activated carbon//\(\text{NaMnO}_2\) assembly between 0 and 1.9 V.\(^{[47]}\) Asymmetric supercapacitors consisting of graphite oxide//\(\text{CuO}\@\text{MnO}_2\) on Ni foils are cycled in 0–1.8 V for 10 000 times with 101.5% capacitance retention in 1 M \(\text{Na}_2\text{SO}_4\) aqueous electrolyte.\(^{[48]}\) Ru films deposited on Ni foam by chemical replacement reaction as both negative and positive electrodes in symmetric supercapacitors are operated for 2000 cycles in 1 M \(\text{Na}_2\text{SO}_4\) without significant capacitance loss in the potential window 0–1.8 V.\(^{[49]}\) Accordingly, Ni can be stably cycled in high potentials with sulfate aqueous electrolytes as current collectors for both negative and positive electrodes.

Complex capacitance analysis is performed on 0.6 mg cm\(^{-2}\) RuO\(_2\)-NDF supercapacitor (Figure 5d,e) by considering it as

![Figure 5. EIS analysis of RuO\(_2\)-NDF with 0.6 mg cm\(^{-2}\) RuO\(_2\). a) Equivalent circuit model with equivalent series resistance (ESR), constant phase element for double layer (CPE\(_{DL}\)) and pseudocapacitance (CPE\(_{P}\)), resistance for charge transfer (\(R_{CT}\)) and leakage (\(R_L\)), and Warburg element (\(W_o\)). Model and experimental Nyquist plot of impedance spectra for b) before cycling and c) after 10000 cycles. Complex capacitance before (0th cycle) and after 10000 cycles for d) imaginary and e) normalized real capacitance.](image)

| Table 1. EIS fitting parameters of RuO\(_2\)-NDF supercapacitor before and after 10 000 cycles. |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|               | ESR (\(\Omega\)) | \(R_{CT}\) (\(\Omega\)) | \(R_L\) (\(\Omega\)) | CPE\(_{DL}\) | CPE\(_{P}\) | \(W_o\) |
| 0th           | 0.665           | 0.15            | 300            | 0.025        | 0.65          | 0.068           | 0.75          | 2         | 0.3     |
| 10 000th      | 0.515           | 0.18            | 120            | 0.04         | 0.62          | 0.039           | 0.83          | 2         | 0.3     |
a whole capacitor with impedance $Z(w) = [jwC(w)]^{-1}$, where $w$ and $C(w)$ are angular frequency and complex capacitance, respectively. The impedance data are obtained directly from EIS measurement. If $Z(w)$ can be expressed as real part $Z’(w)$ and imaginary part $Z”(w)$, complex capacitance can be separated into real part $C’(w)$ and imaginary part $C”(w)$. $C’(w)$ represents available stored energy and $C”(w)$ is responsible for energy loss during charge storage.\cite{51} where $C’(w) = -Z”(w)/[wZ(w)]^2$ and $C”(w) = Z’(w)/[wZ(w)]^2$. Frequency $f_0$ at local maximum of $C’(w)$ specifies dielectric relaxation time constant $\tau_0 = 1/f_0$. Capacitors possess predominately capacitive and resistive behaviors when the frequency is lower and higher than $f_0$, respectively.\cite{51} RuO$_2$-NDF supercapacitor shows higher frequency (5.6 Hz) after 10,000 cycles compared to the 1.3 Hz before cycling, which means the device can be operated in a wider frequency domain and deliver energy faster (from 0.76 s to 0.19 s) after cycling. This agrees with smaller ESR and a wider frequency domain and deliver energy faster (from 0.76 s to 0.19 s) after cycling. This agrees with smaller ESR from cycling, since higher power performance can be delivered with lower ESR in a shorter period.\cite{51} Broader operating frequency range after cycling is also demonstrated in normalized $C’$ (Figure 5e). These measurements suggest the RuO$_2$-NDF supercapacitor can maintain and even slowly improve its performance after long cycles.

Performance of the RuO$_2$-NDF supercapacitors are compared with other two-electrode symmetric supercapacitors by energy density (Wh kg$^{-1}$) and power density (kW kg$^{-1}$) in a Ragone plot (Figure 6). Both energy density and power density are based on the total weight of RuO$_2$ on two electrodes. For 0.3 mg cm$^{-2}$, energy density 60.32 Wh kg$^{-1}$ can be obtained at 0.2 kW kg$^{-1}$, while it decreases to 19.73 Wh kg$^{-1}$ when power density increases to 40 kW kg$^{-1}$. These values are close to those of 0.6 mg cm$^{-2}$ (59.05 Wh kg$^{-1}$ at 0.2 kW kg$^{-1}$, 17.78 Wh kg$^{-1}$ at 40 kW kg$^{-1}$). Energy and power density decrease dramatically for 0.9 mg cm$^{-2}$ (46.73 Wh kg$^{-1}$ at 0.2 kW kg$^{-1}$, 11.11 Wh kg$^{-1}$ at 40 kW kg$^{-1}$) resulting from inefficient utilization of large RuO$_2$ loading. However, the performance of these RuO$_2$-NDF supercapacitors are still close to or even better than most RuO$_2$ composite supercapacitors.\cite{15,18,19,32} Although RuO$_2$ on graphene/CNT foam (RGM)\cite{31} behaves slightly better when power density is beyond 20 kW kg$^{-1}$, high vacuum environment for catalyst deposition and high temperature growth of graphene/CNT foam render RGM impractical for real products. Considering the liquid-based, low temperature, and environmentally friendly process, RuO$_2$-NDF electrodes are relatively facile, inexpensive, and suitable for large scale production.

3. Conclusion

In conclusion, Ni NDF has been demonstrated as an effective current collector for RuO$_2$ nanoparticles. High specific capacitance, high energy and power density, and superior cycling stability over 10,000 cycles can be achieved with RuO$_2$-NDF electrodes. Facile manufacturing processes, including liquid base, low temperature, and environmentally benignity, lead to the possibility of mass production of this novel electrode.

4. Experimental Section

Materials Synthesis: Ni foam (MTI Corp., EQ-bcfn-16m) with 15 mm diameter was first flattened to thickness ~120 μm, and etched in concentrated HCl (EMD, GR ACS, 37%) for 5 min to remove native oxide and increase nucleation cites for Ni nanowire growth. After etching, Ni foam was washed with deionized water for 15 times, and dried on hotplate at 120 °C for 5 min. Average weight loss after HCl etching is ~5 mg. HCl-etched Ni foam was immersed in a 10 mL beaker filled with a solution of 2.5 mL 0.08 M nickel acetate tetrahydrate (Ni(Ac)$_2$··4H$_2$O, Sigma-Aldrich, 98%) in glycerol (Acros, 99%+) heated at 370 °C on a hotplate for 20–40 min without stirring and covered with Al foil to prevent excess solvent evaporation.\cite{21} After growth, Ni nanowires attached on Ni foam were washed with deionized water for 15 times, and dried on hotplate at 120 °C for 5 min. Magnetic field was provided from the magnetic stir rotor inside the hotplate. Ni nanowire weight is ~5.5 mg. Freshly prepared 4 mL solution of 0.3 M oxalic acid dihydrate (ICN Biomedicals Inc., reagent grade) in ethanol (Decon Lab. Inc., 70 proof) with 5 wt% deionized water was used to etch Ni nanowire at 120 °C for 2 h on hotplate into Ni oxalate leaf-like nanostructure,\cite{23} which was further reduced back to Ni nanodendrite in a tube furnace with H$_2$ (50 sccm), Ar (100 sccm) at 20 torr for 10 min at 350 °C with ramping rate 32.5 °C min$^{-1}$. Hydrous RuO$_2$ was prepared with a modified sol–gel method\cite{15,18} with the reaction RuCl$_3$ + 3NaOH = Ru(OH)$_3$ + 3NaCl. 0.8 mL 1 M NaOH (Fisher Scientific, Certified A.C.S.) aqueous solution was dripped dropwise (10 μL per drop) into a 2.3 mL 0.1 M ruthenium chloride hydrate (RuCl$_3$·XH$_2$O, Sigma-Aldrich, ReagentPlus) aqueous solution to reach pH = 7 and stirred for 10 min. The mixed solution was centrifuged and washed with deionized water eight times, and 3.6 mL water was added to make the RuO$_2$ solution concentration ~4 mg mL$^{-1}$. RuO$_2$ solution was dropped onto Ni nanodendrite foam (RuO$_2$-NDF) and dried at room temperature several times until the desired loading was reached. RuO$_2$-NDF composite was annealed at 150 °C for 2 h under vacuum before electrochemical measurement.

Materials Characterization: Surface microstructure and elemental analysis were characterized by scanning electron microscopy (SEM, FEI NovaNanoSEM 450) with energy dispersive X-ray spectroscopy (EDS) detector. Crystalline phase was determined by X-ray diffraction (XRD, PANalytical Empyrean) with Cu-Kα radiation and scan rate 3.5° min$^{-1}$. Nanostructure and crystalline phase were investigated by transmission electron microscopy (TEM, Philips FEI CM300) operated at 300 kV with selected area electron diffraction. TEM samples were prepared by dripping RuO$_2$ nanoparticles dispersed in ethanol onto C film coated TEM grid. Chemical states of RuO$_2$ were examined by X-ray
photoelecotor spectroscopy (XPS, Kratos AXIS ULTRA DLD XPS system) with Al Kα monochromated X-ray source and 165-mm mean radius electron energy hemispherical analyzer.

Electrochemical Characterization: Two-electrode symmetric supercapacitors were prepared with two pieces of RuO$_2$-NDF circular electrodes (dia. 15 mm) separated by two pieces of Celgard 3501 porous membrane (dia. 19 mm) inside a split cell (MTI Corp.) filled with 2M Li$_2$SO$_4$ (≥ 98.5%, Sigma-Aldrich) aqueous electrolyte. Cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) at $E_{\text{ref}} = 0$ V versus open circuit voltage between 0.1 and 1 MHz with amplitude 10 mV were performed. Total capacitance ($C_t$) of the two-electrode capacitor is calculated by $C_t = i/(dV/dt)$, where $i$, $dV$, and $dt$ are current, potential window, and discharge time, respectively. Since the two electrodes are in series, $1/C_t = 1/C_{1} + 1/C_{2}$, where $C_t$ is the capacitance of the single electrode assuming the capacitance of one electrode is very close to the other. Accordingly, $C_{1} = 2C = 2i/(dV/dt)$. Specific capacitance of single electrode ($C_s$) is $C_s = C/m$ where $m$ is the mass of RuO$_2$ of one electrode. Total energy $E = (1/2)C_i(dV)^2$. Total power $P = E/\Delta t$. Both energy density ($E$/2m) and power density ($P$/2m) are based the total weight of RuO$_2$ of the two electrodes.

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

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