Three-dimensional branched single-crystal β -Co(OH)₂ nanowire array and its application for supercapacitor with excellent electrochemical property

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Abstract: We have for the first time fabricated a unique three-dimensional branched single-crystal β -Co(OH)₂ nanowire array supported on Ni foam. This structure is formed by the splitting crystal growth effect combined with the specific topological structure of β -Co(OH)₂. A branched Co₃O₄@MnO₂ core-shell nanowire array is prepared for use as supercapacitor electrode. At a current density of 10 mA cm⁻², the branched Co₃O₄@MnO₂ core-shell nanowire array exhibits 0.99 F cm⁻² of areal capacitance, which is 69.3% of the capacitance (1.43 F cm⁻²) measured at 1 mA cm⁻². In addition, the branched core-shell hybrid can still retain 93.6% of the initial capacitance after 5000 cycles. Such excellent electrochemical performance of the branched Co₃O₄@MnO₂ core-shell nanowire array is attributed to the unique configuration and the strong synergistic effect from the porous Co₃O₄ nanowire core and the ultrathin MnO₂ shell.

Introduction

Supercapacitor, as one of the promising advanced energy storage devices, has attracted considerable attention because it can offer much higher charge/discharge rate than batteries, higher energy density than conventional capacitors, and long

cycle life and environmental friendliness [1,2]. Among various supercapacitor electrode materials, carbon-based supercapacitors store charge from surface electrostatic accumulation in the electric double-layer between the interface of the electrode and the electrolyte [2]. In contrast, transitional metal oxides or hydroxides (e.g., MnO_2 , Co_3O_4 , $\text{Co}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$) store charge by a faradic redox reaction and thus deliver higher specific capacitance [3-10]. However, the unfavorable kinetics and under-utilization of the transitional metal oxides in the charge/discharge process greatly reduce the rate capability, reversibility and stability due to the poor conductivity and the low diffusion coefficient of inserted cations [11-13].

It is known that the use of a polymer binder in the preparation of electrodes inevitably causes considerable “dead volume”, increases the interfacial resistance and retards the electrolyte diffusion, leading to poor capacitive properties [2,11]. Therefore, the strategies for improving the charge and ion transport efficiency need to be developed to enhance energy storage performance. It has been reported that the electrodes with well-organized architectures integrated with conductive substrates could achieve very high capacitive performance [6,14-21]. For example, a highly ordered MnO_2 nanopillar electrode enhanced the surface area nearly 4.5 times compared to that of the planar electrode, the rationally-designed nanostructured electrode for supercapacitor shortened the electron transportation path length and facilitated the rapid diffusion of cations, leading to a 150% enhancement in specific capacitance as well as good charge/discharge ability and cycling stability [20]. Xia et al. designed a hybrid $\text{Co}_3\text{O}_4@\text{Co}(\text{OH})_2$ core-shell nanowire array supported on Ni foam, and this design not only effectively utilized the core and shell, but also achieved a strong synergistic effect [3]. These studies have demonstrated that the microstructure and architecture of a given electrode system can significantly affect its supercapacitive performance.

Branched nanowire heterostructures represent unique nanoscale materials where nanowire branches grow on nanowire backbones, offering interesting optical,

electrical and mechanical properties [22-27]. Ko et al. reported a dye-sensitized solar cell constructed by branched ZnO nanowires; the light-conversion efficiency of the hierarchical ZnO nanostructure was 5 times higher than that of upstanding ZnO nanowires, which was attributed to the reduced charge recombination by direct conduction pathway along ZnO nanotree branches and the enhanced surface area for higher dye loading and light harvesting [24]. Zhou et al. fabricated branched α -Fe₂O₃/SnO₂ nano-heterostructures, in which α -Fe₂O₃ nanorod branches grew on SnO₂ nanowire backbone, the synergistic effect between SnO₂ nanowire and α -Fe₂O₃ nanorod and the characteristic of branched nanostructure enabled the superior performance of the branched α -Fe₂O₃/SnO₂ composite to both α -Fe₂O₃ and SnO₂ individual components in lithium-ion battery application [25]. However, the methods reported for preparing these branched structures typically involve multi-steps and are inefficient [28-33]. For example, a general approach for branched materials synthesis is to use branched nanoporous templates such as anodic aluminum oxide (AAO) templates, but the synthesis of the branched AAO templates consists of consecutive anodization steps [32]. Another general approach for the synthesis of branched materials is to assemble secondary branches on as-prepared nanowire backbones with the assistance of seeds, catalysts and high reaction temperature [24,25,29,33].

In the present work, we have for the first time synthesized a new 3D branched single-crystal β -Co(OH)₂ nanowire array (br-Co(OH)₂) supported on a Ni foam using a one-pot hydrothermal method. The formation mechanism of br-Co(OH)₂ is proposed and discussed. The branched Co₃O₄@MnO₂ core-shell hybrid nanowire array (br-Co₃O₄@MnO₂) is used as a hybrid electrode for supercapacitor application, and the electrochemical properties of the obtained materials are also investigated. In particular, br-Co₃O₄@MnO₂ shows much better capacitive performance as compared with both upstanding Co₃O₄@MnO₂ core-shell nanowire array and 3D branched ZnO@MnO₂ core-shell nanoforest [6,34], and this is attributed to the unique br-Co(OH)₂ nanowire array structure that combines the

high surface area with unimpeded charge and ion transport paths. Our synthesized br-Co(OH)₂ is expected to serve as an excellent scaffold for depositing other capacitive materials for high-performance energy storage devices.

Experimental Section

Synthesis of branched single-crystal β -Co(OH)₂ nanowire array

In a typical synthesis, Ni foam (3 cm × 5 cm in a rectangular shape) was placed in 3 M HCl solution with ultrasonication for 30 min to remove the surface oxide layer and washed with ethanol and water for several times. 10 mmol of Co(NO₃)₂, 20 mmol of NH₄F and 50 mmol of CO(NH₂)₂ were dissolved in 50 mL of distilled water to get a homogeneous precursor solution. The solution was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 65 ml and the Ni foam was subsequently immersed into the precursor solution. The top side of Ni foam was wrapped with a polytetrafluoroethylene tape to prevent the undesired deposition during the synthesis. The autoclave was sealed and heated at 95 °C for 12 h, and then cooled to room temperature naturally. After the resulting pink precursor was taken out of the autoclave and washed with water, br-Co(OH)₂ supported on Ni foam was obtained.

Synthesis of branched Co₃O₄@MnO₂ core-shell hybrid nanowire array and branched Co₃O₄ nanowire array (br-Co₃O₄):

The as-prepared br-Co(OH)₂ was transferred into a 65 ml of Teflon-lined stainless steel autoclave containing 1mM KMnO₄ solution, heated at 160 °C for 30 min and then annealed at 350 °C in air for 2 h to obtain br-Co₃O₄@MnO₂. For comparison, br-Co₃O₄ was also prepared by directly heating br-Co(OH)₂ without immersing in KMnO₄ solution. The weight of br-Co₃O₄@MnO₂ and br-Co₃O₄ grown on Ni foam was measured by calculating the increased mass of Ni foam after reaction and heat treatment. The mass loading of br-Co(OH)₂, br-Co₃O₄ and br-Co₃O₄@MnO₂ was 1.0, 0.8 and 1.3 mg cm⁻², respectively.

Materials characterizations and electrochemical measurements:

The X-ray diffraction (XRD) was conducted on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. The morphology of the composite was examined using a field-emission scanning electron microscope (SEM, JEOL JSM-7100F) and a transmission electron microscope (TEM, JEM-2100) operated at 200 KV with an energy dispersive X-ray spectrometer (EDX). X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Thermo Fisher X-ray photoelectron spectrometer system (ESCALAB250). The electrochemical performance was investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge in 2 M NaOH solution using an Autolab 2 instrument. The nickel foam supported electroactive materials ($\sim 1 \text{ cm}^2$ in area) were directly used as the working electrode. The KCl saturated Ag/AgCl was used as the reference electrode, and graphite rod was used as the counter electrode. EIS measurements were tested in the frequency range from 0.1Hz to 100 kHz at open-circuit potential with an ac perturbation of 0.1 V. The areal capacitance (F cm^{-2}) of the electrodes was calculated based on Equation 1 (CV plots) and Equation 2 (galvanostatic charge/discharge curves), and the specific capacitance of the electrode was calculated by Equation 3:

$$C_a = \frac{\int_{V_a}^{V_c} I(V) dV}{Sv(V_a - V_c)} \quad (1)$$

where C_a is the areal capacitance (F cm^{-2}), S is the geometrical area of the electrode (cm^2), v is the scan rate of CV curves (V s^{-1}), and $(V_a - V_c)$ is the potential window (V).

$$C_a = \frac{I\Delta t}{S\Delta V} \quad (2)$$

where C_a is the areal capacitance (F cm^{-2}), I is the discharge current (A), S is the geometrical area of the electrode (cm^2), ΔV is the potential drop excluding the IR drop (V) and Δt is the total discharge time (s).

$$C_s = \frac{I\Delta t}{m\Delta V}$$

(3)

where C_s is the specific capacitance ($F\ g^{-1}$), I is the discharge current (A), m is the mass of the active materials (g), ΔV is the potential drop excluding the IR drop (V) and Δt is the total discharge time (s).

Results and Discussion

The overall synthetic procedure of 3D br- $Co_3O_4@MnO_2$ involved two steps: (1) br- $Co(OH)_2$ was initially grown on Ni foam through a one-pot hydrothermal process. (2) the as-obtained br- $Co(OH)_2$ was subsequently transferred into a Teflon-lined stainless steel autoclave containing 1 mM $KMnO_4$ solution, heated at 160 °C and finally annealed at 350 °C in air for 2 h. For comparison, 3D branched Co_3O_4 nanowire array (br- Co_3O_4) was also obtained using the similar procedures but without the subsequent coating of MnO_2 shell. XRD analysis (**Figure S1**) indicates that the component of the resulting material (**Figure S1a**) in the first step is brucite-like phase of $\beta-Co(OH)_2$ (JCPDF No. 30-0443). Upon heating in air, the $\beta-Co(OH)_2$ is converted into Co_3O_4 (JCPDF No. 80-1098) (**Figure S1b**). Four new peaks at about 12.8°, 18.1°, 28.8° and 37.5° emerge in br- $Co_3O_4@MnO_2$ (**Figure S1c**), which are assigned to the (110), (200), (310) and (211) planes of MnO_2 (JCPDF No. 44-0141), respectively.

The chemical bonding states of the materials were examined using XPS measurements. As shown in **Figure 1**, the full spectra (**Figure 1a**) shows Mn species presented in br- $Co_3O_4@MnO_2$. In the Co 2p XPS spectrum (**Figure 1b**), besides two shake-up satellite peaks (sat.), a couple of peaks are present in both of Co 2p_{1/2} (796.9 eV/795.3 eV) and Co 2p_{3/2} (782.3 eV/780.4 eV), which are fitted with Co^{2+}/Co^{3+} ions of Co_3O_4 , respectively [35]. The peaks centered at 642.1 eV and 653.8 eV in **Figure 1c** correspond to Mn 2p_{3/2} and Mn 2p_{1/2} spin-orbit states of MnO_2 [36]. The O 1s spectrum (**Figure 1d**) exhibits a new oxygen peak at 529.9 eV compared with that of br- Co_3O_4 (**Figure S2**), which can be assigned to the

oxygen bonded to manganese (Mn-O) of MnO_2 [37]. Two peaks centered at 529.4 eV and 531.0 eV are respectively consistent with oxygen species in Co_3O_4 phase and the presence of OH species adsorbed onto the surface of the nanostructures [38]. The XPS results further confirm Co_3O_4 phase and MnO_2 phase of $\text{br-Co}_3\text{O}_4@\text{MnO}_2$.

Figure 2 shows SEM images of the resulting products on Ni foam at different reaction times. It can be seen that small nanoflakes form on the substrate at the beginning (**Figure 2a**) and grow further as the reaction process continues (**Figure 2b**). When the hydrothermal time is extended to 6 h, interestingly, a series of nanowires appear at the edges of the nanoflakes (indicated by black arrows in **Figure 2c**), showing the nanowire-nanoflake hierarchical configuration composed of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ (JCPDF No. 48-0083) and $\beta\text{-Co}(\text{OH})_2$ (JCPDF No. 30-0443) (**Figure S3b**). In addition, even after 3 h reaction, the nanoflakes without nanowires still contain the $\beta\text{-Co}(\text{OH})_2$ phase (**Figure S3a**), implying the crystal splitting occurs after the generation of $\beta\text{-Co}(\text{OH})_2$. Finally a kind of comb-shaped nanowire is obtained at 12 h (**Figure 2d**). As displayed in **Figure S4**, $\text{br-Co}(\text{OH})_2$ nanowire array densely grows on the Ni foam, and good contact between them can be clearly seen. In the unique nanowire, the branch wires are paralleled with each other attaching to the backbone wire; both the branch and backbone nanowires have a sharp tip and are of about 80 ~ 100 nm in diameter.

In order to gain a better understanding of the morphology and structure evolution on this new branched nanowire array, more detailed experiments and characterization were carried out. Note that nanowires emerge in the nanoflake edge at 4 h, and no other changes are observable in comparison to the morphology at 3 h (**Figure S5b**). However, the needle-like structure forms inside the nanoflakes after 6 h reaction (indicated by white arrows in **Figure 2c**) and rapidly covers the whole nanoflakes (indicated by black arrows in **Figure S5d**). **Figure S5e** shows that two nanowires start to split from the nanoflake at 8 h, and it can be

seen that some branched nanowires still remain the specific interdigitating comb-shaped morphology of the nanowire-nanoflake configuration (**Figure S5f**). **Figure 3a** and **b** show TEM images of br-Co(OH)₂ with its corresponding electron diffraction pattern given in the inset in **Figure 3a**, revealing the single-crystal structure of β -Co(OH)₂. It can be seen that the tip in some nanowires breaks up into two thin nanowires as shown in **Figure 3b**, the tip of the right one is bifurcate as well (**inset, Figure 3b**). Importantly, the phenomenon of splitting is very common in the β -Co(OH)₂ nanowires (**Figure S6a, b**). Previous studies reported that the splitting results in various nanostructures in some materials, such as LnVO₄, TiO₂, Co₃O₄ and Bi₂S₃ [39-42]. Hence the crystal splitting appears to play a very important role in the evolution from nanoflakes to nanowires.

More insights into this interesting phenomenon have been gained when investigating the transition from nanoflake to nanowire; the splitting seems to occur throughout the nanowire formation process. The nanowires marked by the red circle in **Figure 3c** and **Figure S6c** show that the splitting is present in the nanowires stretched out of and inside the nanoflakes. The inset in **Figure 3c** shows the typical electron diffraction pattern of hexagonal single crystal, which is the characteristic feature of crystal splitting [43]. In addition, the nanowires either parallel to each other or form an angle of about 60° or 120° (**Figure 3c, Figure S6d**), which explains the unique comb-like morphology of the final br-Co(OH)₂. Due to the specific hexagonal structure of β -Co(OH)₂, the kinetic growth orientation of β -Co(OH)₂ aligns along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 010 \rangle$ [43]. Consequently the β -Co(OH)₂ preferentially grows along these equivalent directions (**Figure S7**) in accordance with the previous observations [44], resulting in the regular alignment of nanowires angled with 60° or 120° (**Figure S6d**). However, the nanowires angled with other orientations can also be observed, probably due to the asymmetrical distribution and defects of precursor nanoflake in the growth process or the influence of crystal splitting. Splitting is only possible if the oversaturation exceeds a certain critical level that may be driven by a

mechanical factor such as the stress interacted between the nanowire and nanoflake matrix in our case [42], compelling the thin nanowire to deform and rendering one single nanowire to split into two thinner nanowires (**Figure S6e**). The high-resolution TEM (HRTEM) characterization (**Figure 3d**) on the tip of the nanowire is also examined, and the lattice spacing of 0.178 nm (or 0.175 nm) and 0.151 nm corresponds to the (102) and (111) planes of β -Co(OH)₂, respectively. It is found that (102) plane is wrapped, and cracks and some crystal segments near the cracks are generated since the stress in these areas is so concentrated during the crystal splitting that causes the fractures and segments. Particularly, if the stress is much greater than the strength of the crossing nanowire, the nanowire can be broken into several parts (**Figure S6f**), leading to the branched nanowires emerged as the morphology without the interdigitating comb-shaped structure, consistent with the structure in **Figure 2d**.

Based on the above discussions, the growth mechanism on this unique branched nanowire has been proposed and shown in **Figure S8**. At the beginning, Co²⁺ ion was converted into the CoF_x^{(x-2)-} by incorporating F⁻. When the temperature reached around 70 °C, the hydrolysis-precipitation process of urea proceeded, and CO₃²⁻ and OH⁻ anions were then gradually produced into the precursor solution, enabling the complex CoF_x^{(x-2)-} to release Co²⁺ [45]. When Co²⁺ ions were supersaturated, they tended to align themselves with specific orientations to form planar structure on the Ni foam (**Figure S8a, b**). When more Co²⁺ ions were released in the reaction solution, the planar nuclei grew up and the nanoflakes were fully grown on the surface of Ni foam. In the second step, the crystal splitting occurred after β -Co(OH)₂ was generated in the nanoflakes (**Figure S3**), β -Co(OH)₂ nanowire crystals started to nucleate at the edges of the nanoflakes (**Figure S8c**) and align themselves with three equivalent specific orientations (<100>, <110> and <010>) due to their specific hexagonal structure. With the reaction proceeding, the stress accumulated at the interface of the nanowires and nanoflake matrix until it reached a critical value where the nanowires would

separate themselves from each other and the splitting took place. Therefore the nucleation and growth process integrating with crystal splitting of $\beta\text{-Co(OH)}_2$ enabled the regular alignment of nanowires angled with 60° or 120° (**Figure S8d**) and finally formed the unique branched structure (**Figure S8e**). The stress could even tear the crossing nanowire into several segments, and the balance between stress and the strength of crossing nanowire determined the resulting structure. If the strength of nanowire was stronger than the stress, the branched nanowires showed an interdigitating comb-shaped morphology (**arrow B, Figure S8f**); otherwise the comb-like structure shown in **Figure 2d** was formed eventually (**arrow A, Figure S8f**). **Figure S9** shows a planar grid-like structure deposited on Ni foam, probably transformed from the exfoliated nanoflake, implying that the branched structure obtained in our study is only part of the transformational branched nanowires that have a good contact with Ni foam substrate, while the others might have fallen off into the solution. It is believed that the specific topological structure of $\beta\text{-Co(OH)}_2$ and the crystal splitting growth play important roles in the formation of the branched structure; crystal splitting and the cracks in the nanowires are supposed to be the release of accumulated stress during the growth process. However, the formation of the nanoflakes at the initial stage has not been fully understood yet, and it is still unclear how crystal growth combined with crystal splitting affects the transformation process from nanoflakes to nanowires. Therefore further studies on the structural evolution are needed.

MnO_2 and Co_3O_4 have been widely employed for the supercapacitor application due to the natural abundance, cost-effectiveness, environmental benignness and high theoretical specific capacitance [5,12,46-48]. Moreover, rational design of the hybrid composite could manifest the electroactivity of each component and the strong synergistic effect has achieved superior capacitive performances to single oxides [6]. Therefore, we have prepared the hybrid $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ by in-situ growth of a MnO_2 layer on branched nanowires, and $\text{br-Co}_3\text{O}_4$ has also been synthesized after annealing treatment in the furnace for comparison with

br-Co₃O₄@MnO₂. After annealing, br-Co₃O₄ is obtained with good contact with the Ni foam (**Figure S10**). br-Co₃O₄ retains the branched morphology of br-Co(OH)₂ precursor (**Figure 4a**), and the nanowires in br-Co₃O₄@MnO₂ shows an increase in diameter (**Figure 4b**) and the core nanowire is visibly coated by a layer of nanoflakes (**inset, Figure 4b**). **Figure 4c** shows that br-Co₃O₄ is a porous structure that has the high surface area, favoring the efficient contact between Co₃O₄ and electrolytes and offering more active sites for the electrochemical reactions [49]. The HRTEM image in the inset of **Figure 4c** reveals the interplanar spacing of 0.146 nm and 0.209 nm, corresponding to the (440) and (400) planes of Co₃O₄, respectively. The energy dispersive X-ray spectroscopy (EDX) mapping images of elemental distribution (**Figure S11**) further verified that Mn species are present in br-Co₃O₄@MnO₂, consistent with the previous XPS spectra in **Figure 1**. Furthermore, br-Co₃O₄@MnO₂ displays the hierarchical configuration with porous Co₃O₄ nanowire as core and thin MnO₂ nanoflakes (about 4 ~ 9 nm thick) as shell (**Figure 4d**), and the lattice spacing of 0.69 nm could be assigned to the (110) plane of MnO₂ (**inset, Figure 4d**).

The electrochemical properties of br-Co₃O₄ and br-Co₃O₄@MnO₂ have been examined in a three-electrode configuration using an Autolab 2 instrument in 2 M NaOH aqueous solution. **Figure 5a** shows the CV plots ranged from -0.1 to 0.5 V at a scan rate of 2 mV s⁻¹. A pair of redox peaks A/A' at 0.33 V and 0.12 V (vs Ag/AgCl) can be observed for br-Co₃O₄@MnO₂, due to the surface Faradic effect described as follows [38]:

In addition, the CV plot of br-Co₃O₄@MnO₂ expands and has a larger enclosed area than that for br-Co₃O₄ due to the present of MnO₂ nanoflakes, stemming from the intercalation/extraction of protons (H₃O⁺) or alkali cations (K⁺) into the oxide [17], indicating that the hierarchy architectural br-Co₃O₄@MnO₂ enables better energy storage ability than br-Co₃O₄. The CV plots at different scan rates for

br-Co₃O₄@MnO₂, br-Co₃O₄ and br-Co(OH)₂ are shown in **Figure 5b**, **Figure S12a** and **Figure S12b**, respectively. The areal capacitance values as a function of scan rate are provided in **Figure S12c**. br-Co₃O₄ shows a slightly better capacitance than br-Co(OH)₂ owing to the porous structure (**Figure 4c**), and br-Co₃O₄@MnO₂ exhibits the best capacitance, specifically 0.987, 0.824 and 0.633 F cm⁻² at the respective scan rate of 2, 5 and 10 mV s⁻¹. Therefore, the contribution of Ni foam (20 mF cm⁻²) to the total capacitance could be ignored (**Figure S12d**).

The galvanostatic charge–discharge measurements are carried out to further estimate the capacitive performance. As shown in **Figure 5c**, at a current density of 1 mA cm⁻², br-Co₃O₄@MnO₂ hybrid shows the capacitance of 1.43 F cm⁻², higher than 0.68 F cm⁻² for br-Co₃O₄ owing to its well-designed core-shell structure that maximizes the utilization of both components, where the porous Co₃O₄ nanowires enwrapped by MnO₂ nanoflakes participate into the redox reaction, as indicated from the higher redox peaks of A/A' in the CV plots (**Figure 5a**). In addition, br-Co₃O₄@MnO₂ shows a decrease of IR drop (0.025 V) in contrast with br-Co₃O₄ (0.048V), implying superior charge transport of br-Co₃O₄@MnO₂ which will be beneficial to the rate capacity of the electrode, as confirmed by the electrochemical impedance spectra shown in **Figure 5d**. Since the straight line corresponds to the diffusive resistance (Warburg impedance) related to the diffusion of the electrolyte within the pores of the electrode, interestingly, both of br-Co₃O₄ and br-Co₃O₄@MnO₂ have the same diffusion resistance, indicating that Co₃O₄ nanowire core can still be accessed by OH⁻ and contribute to the electron storage, in good agreement with the CV observations (**Figure 5a**). **Figure 5e** and **Figure S12h** (extracted from **Figure S12 e, f and g**) illustrates the capacitance of both hybrid, pristine br-Co₃O₄ and br-Co(OH)₂. Within the current density varying from 1 to 20 mA cm⁻², the hybrid array delivers the areal capacitance 2 ~ 4 times higher than br-Co₃O₄ and br-Co(OH)₂ array. Furthermore, the areal capacitance of the hybrid (0.99 F cm⁻²) at 10 mA cm⁻²

maintains up to 69.3% of that measured at 1 mA cm^{-2} (1.43 F cm^{-2}) in contrast with 44.1% for $\text{br-Co}_3\text{O}_4$, indicating that the $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ hybrid exhibits better rate capability than $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ as predicted by **Figure 5c** and **d**. MnO_2 -based hybrids have been prepared and investigated in previous studies [17,34,44]. For example, MnO_2 was deposited on a 3D ZnO nanoforest to form a core-shell hybrid with the capacitance of 31.30 mF cm^{-2} at 0.02 mA cm^{-2} [34]. Although the high surface area and electron transport efficiency of branched structure was maintained, the much smaller contribution to capacitance from branched ZnO nanowire core leads to the worse charge storage performance. A well-ordered Te nanowire array growth on carbon cloth is used as template for the MnO_2 loading, the resulting Te/Au/MnO_2 core-shell nanowire array shows the capacitance of 35.83 mF cm^{-2} at the current density of 4 mA/cm^{-2} [17]. A new type of two-dimensional $\beta\text{-MnO}_2$ nanowire network exhibits a specific capacitance of 453.0 F g^{-1} at a current density of 0.5 A g^{-1} [44]. In contrast, by using $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ hybrid we have achieved much better energy storage ability with the specific capacitance of 1072.6 F g^{-1} (1.4 F cm^{-2}) at 1.54 A g^{-1} (2 mA cm^{-2}) and 592.3 F g^{-1} (0.77 F cm^{-2}) even at 15.4 A g^{-1} (20 mA cm^{-2}); this is superior to that of the reported upstanding $\text{Co}_3\text{O}_4@\text{MnO}_2$ core-shell nanowire array (0.56 F cm^{-2} at 11.25 mA cm^{-2} , 480 F g^{-1} at 2.67 A g^{-1}) [6], which is originated from the enlarged surface area and improved charge transport of branched structure. Compared with other CoO_x -based hybrids [50,51], our $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ core-shell hybrid shows a higher or comparable capacitance, which demonstrates that the synthesized br-Co(OH)_2 can be an excellent scaffold for preparing well-ordered hybrid for use as high-performance supercapacitor electrode.

The cycling stability of the hybrid nanowire array by repeating charging–discharging processes was recorded and presented in **Figure 5f**. It can be clearly seen that both the areal capacitance and cycling stability are significantly enhanced for the $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ hybrid electrode. At a current density of 8 mA cm^{-2} , the overall capacitance loss for br-Co(OH)_2 (**Figure S12i**) and $\text{br-Co}_3\text{O}_4$ is

about 67.6% and 55.7% after 5000 cycles, respectively, while br-Co₃O₄@MnO₂ can retain 93.6% of the initial capacitance. On one hand, MnO₂ nanoflake shell prevents the Co species of core from dissolving in the electrolyte solution [52]; on the other hand, since the contact between nanowire array and Ni foam substrate becomes weaker due to the volume changes resulted from phase variation during the charge-discharge process, MnO₂ shell enwrapped on the Co₃O₄ surface stabilizes the mechanical connection and improves the electrode structural integrity [5,6]. In the beginning several hundred cycles, the capacitance increases with the repeated cycling, which is considered as an activating process [49,53]. The highest capacitance values from br-Co(OH)₂ and the pristine br-Co₃O₄ in the cycling test are 0.46 and 0.39 F cm⁻², which is still much lower than 1.03 F cm⁻² for br-Co₃O₄@MnO₂ hybrid even after 5000 cycles, indicating the good electrochemical stability of the hybrid for long cycling life application. The enhanced electrochemical performance of br-Co₃O₄@MnO₂ is attributed to its unique novel configuration: first, br-Co₃O₄ converted from br-Co(OH)₂ on conductive Ni foam serves as a scaffold and has good conductivity for charge storage and delivery; second, the hierarchically porous br-Co₃O₄@MnO₂ structure results in high electrode/electrolyte interfaces; third, well-ordered br-Co₃O₄@MnO₂ is strongly supported on Ni foam avoiding the use of polymer binder and conductive additives, significantly reducing the inactive interfaces; forth, the ultrathin MnO₂ nanoflake shell wrapped on the br-Co₃O₄ surface not only allows ion penetration into the core, but also shortens the electron transportation path and stabilizes the structural integrity of the core in charge-discharge process; and fifth, both the br-Co₃O₄ core and MnO₂ nanoflake shell materials are good active materials.

Conclusions

A novel unique branched single-crystal β -Co(OH)₂ nanowire array supported on Ni foam was fabricated by a simple one-pot synthesis. The formation mechanism was discussed in which the specific topological structure of β -Co(OH)₂ and crystal

splitting in the growth process was presumably responsible for the unique branched structure. The branched nanowire array was used as a scaffold to construct br-Co₃O₄@MnO₂ core-shell hybrid for supercapacitor application. The hybrid achieved the capacitance of 0.99 F cm⁻² at a current density of 10 mA cm⁻² with excellent rate capacity and long-term cycling stability. The enhanced capacitive performance of the br-Co₃O₄@MnO₂ hybrid could be attributed to the unique br-Co(OH)₂ scaffold and the strong synergetic effect of core-shell structure, which not only maximized the utilization of both components, but also enlarged the surface area, shortened the ion transportation path and favored the charge collection and mechanical stabilization. This novel br-Co(OH)₂ can be potentially applied as high-performance electrode for supercapacitor and components in other electrochemical devices.

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Figure 1. (a) XPS full spectra of br-Co₃O₄ (1) and br-Co₃O₄@MnO₂ (2); High-resolution XPS spectra of br-Co₃O₄@MnO₂: Co 2p (b), Mn 2p (c) and O 1s (d).

Figure 2. SEM images of br-Co(OH)₂ nanowire array on Ni foam at different reaction time: 1 h (a), 3 h (b), 6 h (c) and 12 h (d).

Figure 3. TEM images of the nanowires at 12h (a) (b); TEM image of resulting materials obtained (c) at 6 h and its corresponding HRTEM image (d) of the nanowire tip marked by white rectangle in (c). The insets in (a) (c) show their corresponding electron diffraction patterns respectively; the inset in (b) shows the large-magnification image of the circled area of (b); the red cycles show the splitting happening at the tip of nanowires; the red arrows in (d) show the crack in the nanowire and the black cycled areas show the crystal segments resulting from the splitting.

Figure 4. SEM images of br- Co_3O_4 (a) and br- $\text{Co}_3\text{O}_4@\text{MnO}_2$ (b); TEM images of br- Co_3O_4 (c) and br- $\text{Co}_3\text{O}_4@\text{MnO}_2$ (d). The insets in (a) (b) show the corresponding high-magnification SEM images; the insets in (c) (d) show the HRTEM images of Co_3O_4 nanowires and MnO_2 nanoflakes, respectively.

Figure 5. CV plots of $\text{br-Co}_3\text{O}_4$ and $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ at the scan rate of 2 mV s^{-1} (a); CV plots of $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ at different scan rates (b); galvanostatic charge-discharge curves of $\text{br-Co}_3\text{O}_4$ and $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ at 1 mA cm^{-2} (c); Nyquist plots at the range of $0.1 \text{ Hz} \sim 100 \text{ KHz}$ (d); capacitance as a function of current density for $\text{br-Co}_3\text{O}_4$ and $\text{br-Co}_3\text{O}_4@\text{MnO}_2$ (e); the corresponding cycling stability at the current density of 8 mA cm^{-2} (f).