Tuning the morphology of Co3O4 on Ni foam for supercapacitor application

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Abstract
In this work, NH4F was used as a vital additive to control the morphology of Co3O4 precursors on Ni foam in a conventional hydrothermal reaction, and then, via thermal decomposition, to obtain Co3O4 material. The amount of NH4F plays a pivotal role in the formed morphology of the Co3O4 precursors, and four morphologies of Co3O4 were obtained through close control of the amount of additive: nanowires, thin nanowire-clusters, thick nanowire-clusters, and fan-like bulks. The morphological evolution process of the Co3O4 precursors has been investigated according to their intermediates at different reaction stages, and some novel growth mechanisms are proposed: (1) the amount of NH4F in the solution system affects the chemical composition of the precursors; (2) with an increasing amount of NH4F in the solution system, the morphology will tend to form more ordered states and more distinct hierarchical structures; (3) with an increasing amount of NH4F in the solution system, the growth of products will tend to form denser structures; (4) the amount of NH4F in the solution system will affect the mass loading of products. The four different morphologies of Co3O4 were tested as free-standing electrode materials for supercapacitor application. Co3O4 with the thin-nanowire-cluster morphology exhibits the best electrochemical performance: the specific area capacitance is 1.92 F cm-2 at the current density of 5 mA cm-2 and goes up to 2.88 F cm-2 after 3000 charge-discharge cycles, while the rate capability is 72.91% at the current density of 30 mA cm-2.

Keywords
Co3O4, Ni, morphology, foam, supercapacitor, application, tuning

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Tuning the morphology of Co$_3$O$_4$ on Ni foam for supercapacitor application†

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In this work, NH$_4$F was used as a vital additive to control the morphology of Co$_3$O$_4$ precursors on Ni foam in a conventional hydrothermal reaction, and then, via thermal decomposition, to obtain Co$_3$O$_4$ material. The amount of NH$_4$F plays a pivotal role in the formed morphology of the Co$_3$O$_4$ precursors, and four morphologies of Co$_3$O$_4$ were obtained through close control of the amount of additive: nanowires, thin nanowire-clusters, thick nanowire-clusters, and fan-like bulks. The morphological evolution process of the Co$_3$O$_4$ precursors has been investigated according to their intermediates at different reaction stages, and some novel growth mechanisms are proposed: (1) the amount of NH$_4$F in the solution system affects the chemical composition of the precursors; (2) with an increasing amount of NH$_4$F in the solution system, the morphology will tend to form more ordered states and more distinct hierarchical structures; (3) with an increasing amount of NH$_4$F in the solution system, the growth of products will tend to form denser structures; (4) the amount of NH$_4$F in the solution system will affect the mass loading of products. The four different morphologies of Co$_3$O$_4$ were tested as free-standing electrode materials for supercapacitor application. Co$_3$O$_4$ with the thin-nanowire-cluster morphology exhibits the best electrochemical performance: the specific area capacitance is 1.92 F cm$^{-2}$ at the current density of 5 mA cm$^{-2}$ and goes up to 2.88 F cm$^{-2}$ after 3000 charge–discharge cycles, while the rate capability is 72.91% at the current density of 30 mA cm$^{-2}$.

1. Introduction

Spinel oxide Co$_3$O$_4$, as an important kind of p-type semiconductor material, has attracted more and more attention due to its wide applications in field emission,$^1$ heterogeneous catalysis,$^2$ electrochromic devices,$^3$ magnetic materials,$^4$ biosensors,$^5$ gas sensors,$^6$ supercapacitors,$^7$ and Li-ion batteries.$^8$ So far, many different morphologies have been fabricated for Co$_3$O$_4$ nanomaterials, such as nanowalls,$^9$ nanosheets,$^{10}$ nanotubes,$^{11}$ nanocubes,$^{12}$ nanonets,$^{13}$ nanorods,$^{14}$ nanospheres,$^{15}$ nanobelts,$^{16}$ nanoplates,$^{17}$ nanomeshes,$^{18}$ etc., in order to enhance the performance of Co$_3$O$_4$ in a particular application area.

Nowadays, energy storage and conversion materials have become an important research subject because of the increasing global demand for energy. Compared with Li-ion batteries, supercapacitors have the unique merits of good pulsed charge–discharge characteristics, high power density, and long lifetime, making them applicable and indispensable in many portable systems and hybrid electric vehicles.$^{19,20}$ Co$_3$O$_4$ has been considered as a promising electrode material for supercapacitors owing to its high theoretical capacitance, well-defined redox activity, great reaction reversibility, low fabrication cost, natural abundance, and environmental friendliness.$^{21}$

A free-standing high specific capacitance electrode should be the most promising type of electrode for potential practical applications in the future, because such electrodes allow highly efficient industrial production, since the active materials do not need to be mixed with carbon black (conductive agent) or polyaniline dihydroxide (PVDF) binder. Among the many synthesis methods for Co$_3$O$_4$, hydrothermal reaction could satisfy the above requirements, and it also could be suitable for large-scale production.$^{22}$ The mass loading of Co$_3$O$_4$ on Ni foam through hydrothermal reaction is limited, however, which renders relatively low area capacitance. NH$_4$F could be a potential promoter of mass loading on the current collector during the hydrothermal reaction, while which could affect the morphology.

In this report, four morphologies of Co$_3$O$_4$ on Ni foam were obtained through conventional hydrothermal reaction to fabricate the precursor, and then, via thermal decomposition reactions, the final product. During the hydrothermal reaction, different amounts of NH$_4$F were applied as an additive, and it

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was found that the NH$_4$F plays a pivotal role in forming the morphology of the Co$_3$O$_4$ precursors, so that four different morphologies were obtained: nanowires, thin nanowire-clusters, thick nanowire-clusters, and fan-like bulks. Furthermore, the morphological evolution process of the Co$_3$O$_4$ precursors was investigated according to their intermediates in different reaction stages, and some novel growth mechanisms are proposed: firstly, the amount of NH$_4$F applied in the solution system affects the chemical composition of the precursor. With a low amount of NH$_4$F, the precursor is Co(CO$_3$)$_{0.5}$(OH)$_{0.7}$. Secondly, with increasing amounts of NH$_4$F in the solution system, the morphology will tend to form more ordered states and more distinct hierarchical structures, from nanowires to thin nanowire-clusters, to thick nanowire-clusters, and then to fan-like bulks. Thirdly, with increasing amounts of NH$_4$F in the solution system, the final products tend to form denser structures. Nanowires tend to stack together with the medium amount of NH$_4$F, and the gaps among nanowires are reduced significantly compared with the sparsely distributed nanowires that are obtained with a small amount of NH$_4$F. With a high amount of NH$_4$F, the nanowires are replaced by nanosheets, which further promote a dense structure. Fourthly, the amount of NH$_4$F in the solution system affects the mass loading of products on the Ni foam substrate. On introducing a medium amount of NH$_4$F into the solution system, the mass loading on Ni foam will increase notably compared with that with a low amount of NH$_4$F, although the mass loading on Ni foam does not increase linearly as the amount of NH$_4$F increases, and a high amount of NH$_4$F suppresses further increases in the mass loading on Ni foam. The electrochemical performances of the four different morphologies of Co$_3$O$_4$ as free-standing electrode materials were tested for supercapacitor application. Co$_3$O$_4$ with the thin-nanowire-cluster morphology exhibits the best electrochemical performance among the four electrodes: the specific area capacitance is 1.92 F cm$^{-2}$ at the current density of 5 mA cm$^{-2}$, rising to 2.88 F cm$^{-2}$ after 3000 charge–discharge cycles, and the rate capability is 72.91% at the current density of 30 mA cm$^{-2}$. Its high specific area capacitance makes it an ideal potential supercapacitor electrode for practical application.

2. Experimental

2.1 Synthesis of Co$_3$O$_4$ on Ni foam

All the chemical reagents were of analytical grade and were used without further purification. Ni foam (1 cm × 3 cm) was cleaned with acetone in an ultrasound bath for 5 min, rinsed with deionized water, immersed in 6 M hydrochloric acid for 3 min to remove any possible surface oxide layer, and finally rinsed with deionized water. 1 mmol CoCl$_2$·6H$_2$O, 10 mmol urea, and different amounts of NH$_4$F (1 mmol, 5 mmol, 10 mmol, and 20 mmol, respectively) were dissolved in 18 ml deionized water to form a homogeneous solution. The solutions were transferred into a 25 mL Teflon-lined stainless-steel autoclave, and the pretreated Ni foam substrates were inserted vertically into the autoclaves. The autoclaves were maintained at 115 °C for 6 h and then naturally cooled down to room temperature. The precursor samples were washed with deionized water several times to remove the residual reactants and free debris, and then dried at 80 °C for 12 hours. Finally, the obtained precursors were annealed at 300 °C for 3 hours in air with a ramping rate of 2 °C min$^{-1}$ to transform the precursor into Co$_3$O$_4$. The corresponding samples synthesised by adding 1 mmol, 5 mmol, 10 mmol, and 20 mmol NH$_4$F were denoted as Co$_3$O$_4$-1, Co$_3$O$_4$-2, Co$_3$O$_4$-3, and Co$_3$O$_4$-4, respectively.

2.2 Materials characterization

Scanning electron microscope (SEM) images were collected by a field-emission scanning electron microscope (FESEM, JEOL-7500, 2 keV). X-ray diffraction (XRD) patterns were collected on a polycrystalline X-ray diffractometer (RIGAKU, D/MAX 2550 VB/PC, 40 kV/20 mA, λ = 1.5406 Å). Transmission electron microscope (TEM) images and high-resolution transmission electron microscope (HRTEM) images were collected on a transmission electron microscope (JEOL-2010, 200 keV). Fourier transform infrared (FTIR) spectrum was collected on a spectrophotometer (Nicolet Nexus 470).

2.3 Electrochemical performance measurements

The electrochemical performance of the as-prepared electrodes was measured using cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) testing, and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (VMP-3) with a typical three-compartment cell at ambient temperature. In the three-compartment cell, the Co$_3$O$_4$ electrode was used as the working electrode, platinum plate was used as the counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode. EIS testing was performed in the frequency range from 0.01 Hz to 100 kHz at the open circuit potential by applying a sinusoidal waveform with an amplitude of 5 mV. 2.0 M KOH solution was used as the electrolyte.

3. Results and discussion

SEM images of the different morphologies of Co$_3$O$_4$ are shown in Fig. 1a–h. Fig. 1(a and b) shows the morphology of Co$_3$O$_4$-1, and it can be seen that there are many nanowires covering the Ni foam in a disordered state. Fig. 1(c and d) shows the morphology of Co$_3$O$_4$-2, which is very different from the morphology of Co$_3$O$_4$-1, as some nanowires are now stacked together, taking on the shape of thin nanowire-clusters, which represent hierarchical structure to some extent. Compared with Co$_3$O$_4$-2, in Fig. 1(e and f), the morphology of Co$_3$O$_4$-3 with Co$_3$O$_4$-2, in Fig. 1(e and f), the morphology of Co$_3$O$_4$-3 features a thick nanowire-cluster structure, which means that every nanowire-cluster consists of more nanowires, which renders the hierarchical structure more distinct and thus leads to a more ordered state. It is noticeable that the morphologies of Co$_3$O$_4$-1, Co$_3$O$_4$-2, and Co$_3$O$_4$-3 share some common characteristics: their basic construction unit is the nanowire. The diameters of these nanowires are in the range of 100–150 nm. It also should be
noted that the nanowires of Co₃O₄-2 and Co₃O₄-3 on Ni foam are denser than those of Co₃O₄-1. In Fig. 1(g and h), the morphology of Co₃O₄-4 is totally different from the above three morphologies: it shows some fan-like bulks appearing on the Ni foam. With a closer view, the fan-like bulks are clearly composed of many nanosheets rather than nanowires, and they also display hierarchical structure. To the best of our knowledge, the morphologies of Co₃O₄-3 and Co₃O₄-4 have never been reported previously.

In Fig. 2, the XRD patterns reveal the crystal structure and phase purity of as-obtained Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4. The two highest intensity peaks at 44.5° and 51.8° are ascribed to the (111) and (200) planes of metallic nickel (JCPDS no. 04-0850), respectively. The peaks at 31.4°, 36.9°, 59.3°, and 65.2° in the four patterns belong to the (220), (311), (511), and (440) planes of Co₃O₄ (JCPDS no. 42-1467).

Further morphology and structure characterizations were conducted by TEM, as shown in Fig. 3. In Fig. 3(a, c, and e), the TEM images reveal the basic construction units to be nanowires in Co₃O₄-1, Co₃O₄-2, and Co₃O₄-3, respectively. It can be seen that these nanowires are highly porous, being composed of interconnected nanoparticles approximately 10–25 nm in size. The diameters of these nanowires are in the range of 100–150 nm, which is in accordance with those observed in the SEM images. From Fig. 3d, it can be seen that the basic construction unit of Co₃O₄-4 is the nanosheet, with a size in the range of 300–500 nm. The nanosheets display some wrinkling. From the HRTEM images in Fig. 3(b, d, f, and h), the (111), (220), and (400) interplane spacings of 0.47, 0.29, and 0.21 nm respectively correspond to the different crystallographic planes of Co₃O₄, as indicated, which also matches well with the XRD diffraction results.

4. Growth analysis and formation mechanism

Fig. 4 shows the evolution process for the precursors of Co₃O₄-1 (1 mmol NH₄F), Co₃O₄-2 (5 mmol NH₄F), Co₃O₄-3 (10 mmol NH₄F), and Co₃O₄-4 (20 mmol NH₄F), for reaction times of 20 min, 1 h, 2 h, and 4 h. On introducing a low amount of NH₄F (1
mmol), at 20 min into the initial stage (Fig. 4a), nanoflake clusters cover the nickel foam. When the reaction time was prolonged to 1 h (Fig. 4b), there were nanowires covering the nickel foam. After 2 h reaction (Fig. 4c), the Ni foam was totally covered by nanowires, and the nanowires became longer and slimmer. After 4 h (Fig. 4d), however, there was no apparent difference in morphology between 2 h and 4 h, which indicates that the nanowires had finished their growth by 2 h. On introducing a medium amount of NH₄F (5 and 10 mmol) and a high amount of NH₄F (20 mmol), the morphology evolution process became complicated. At 20 min into the initial stage (Fig. 4e, i, and m), nanoflakes covered the nickel foam, but the nanoflakes with 10 and 20 mmol of NH₄F were more ordered than those with 5 mmol of NH₄F. After 1 h, some bulks composed of nanoflakes protruded on the Ni foam (Fig. 4f, j, and n), but those bulks with 10 or 20 mmol of NH₄F were thicker than with that with 5 mmol. When the reaction time was prolonged to 2 h, those bulks still protruded on the substrate, but they had become bigger and denser (Fig. 4g, k, and o), and the thickness of the bulks with 10 and 20 mmol of NH₄F was still greater than that with less NH₄F (5 mmol). After 4 h, the morphologies with medium amounts (5 and 10 mmol) of NH₄F evolved from bulks into nanowire-clusters (Fig. 4h and l), which reveals the reason why clusters with 10 mmol of NH₄F contained more nanowires than those with 5 mmol. The thickness of the nanowire clusters is dependent on the thickness of the initial formative bulks. As for the morphology of bulks with a high amount of NH₄F (20 mmol), the bulks (Fig. 4p) did not evolve into nanowire-clusters after 4 h and even after 6 h (Fig. 2g and h). Compared with the samples with 5 and 10 mmol of NH₄F, they still kept the bulk-like structure, but after 6 h, the bulk was composed of nanosheets (Fig. 2g and h) rather than nanoflakes, and its final structure was denser than for the other three counterparts. In addition, the growth of nanowires with the lowest amount of NH₄F (1 mmol) leads to a disordered state, while the growth of nanowire clusters with medium amounts of NH₄F (5 and 10 mmol) displays relatively ordered behaviour, although the growth of nanowire clusters with 10 mmol of NH₄F is more ordered than that of nanowire-clusters with 5 mmol of NH₄F, and the hierarchical structure becomes more distinct. It should

Fig. 4 Pathways of morphology evolution shown in SEM images of the corresponding precursors of Co₃O₄-1 (a–d), Co₃O₄-2 (e–h), Co₃O₄-3 (i–l), and Co₃O₄-4 (m–p) for different reaction times: 20 min, 1 h, 2 h, and 4 h.
be noted that the bulks with the highest amount of NH₄F (20 mmol) also exhibit an ordered state and hierarchical structure, with the nanowires merely replaced by nanosheets.

Based on the above descriptions, it could be concluded that the amount of NH₄Faffects the morphology of the Co₃O₄ precursor during the hydrothermal reaction process. The most direct reason is that the compositions of the precursors for the different samples are different. From the XRD patterns of these precursors after the 6 h hydrothermal reaction (Fig. S1 and S2 in ESI†), the precursor with the lowest amount of NH₄F (1 mmol) is Co(CO₃)₀.₅(OH)₀.₁₁H₂O, while the precursors with medium amounts of NH₄F (5 and 10 mmol) and the highest amount of NH₄F (20 mmol) are CoF₁.₃(OH)₀.₇, which could explain our observations that introducing medium amounts of NH₄F (5 and 10 mmol) or a high amount of NH₄F (20 mmol) makes the morphology evolution process more complicated. The composition of Co₃O₄-1 precursor was further investigated by measuring a FTIR spectrum from 400 to 4000 cm⁻¹ (Fig. S3 in ESI†). The peaks at 3501 and 1518 cm⁻¹ are ascribed to O–H stretching vibration and bending vibration, respectively, the peaks at 1383 and 1070 cm⁻¹ arise from CO₃²⁻ asymmetrical and symmetrical stretching vibration, respectively, and the peaks at 834 and 693 cm⁻¹ are assigned to out-of-plane and in-plane bending vibration of CO₃²⁻, respectively. From some previous reports, it is generally considered that F⁻ anions could slow down the nucleation rate and activate the substrate, because F⁻ ions can coordinate with Co²⁺ ions at the initial stage and then release the Co²⁺ ions slowly, but from this work, when there are medium amounts of NH₄F (5 and 10 mmol) or a high amount of NH₄F (20 mmol) in the solution system, the precursor product is CoF₁.₃(OH)₀.₇, which could explain the greater complication of the morphology evolution process. With a medium (5 or 10 mmol) or high (20 mmol) amount of NH₄F in the solution system, the F⁻ not only takes part in the reaction, but also forms the stable precursor product CoF₁.₃(OH)₀.₇. This also suggests that the formation of CoF₁.₃(OH)₀.₇ helps to reduce the nucleation rate to some extent, making the morphologies with 5 and 10 mmol of NH₄F experience an evolution from bulks to nanowire clusters. It should be noted that 20 mmol of NH₄F hinders the formation of nanowires, and the bulks directly evolve into nanosheets, thus reducing the interspaces among the nanowires, which further reveals that F⁻ could slow down the nucleation rate and make the structure denser. The corresponding mechanisms for the effects of different amount of NH₄F on the morphology are proposed, as shown in Fig. 5. The hydrothermal chemical reaction could be suggested as follows:

\[
\begin{align*}
\text{Co}^{2+} + x\text{F}^- & \rightarrow [\text{CoF}_x]^{(x-2)-} \\
\text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} & \rightarrow 2\text{NH}_3 + \text{CO}_2 \\
\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{OH}^- \\
2[\text{CoF}_x]^{(x-2)-} + \text{CO}_3^{2-} + 2\text{OH}^- + x\text{H}_2\text{O} & \rightarrow \text{Co}_2(\text{OH})_2\text{CO}_3 \cdot x\text{H}_2\text{O} + 2x\text{F}^- \\
[\text{CoF}_x]^{(x-2)-} + \text{OH}^- & \rightarrow \text{Co(OH)F} + (x-1)\text{F}^- \\
\end{align*}
\]

Subsequently, the precursors are transformed to stable Co₃O₄ phase in air.

\[
\begin{align*}
3\text{Co}_2(\text{OH})_2\text{CO}_3 \cdot n\text{H}_2\text{O} + \text{O}_2 & \rightarrow 2\text{Co}_3\text{O}_4 + (3n + 3)\text{H}_2\text{O} + 3\text{CO}_2 \\
6\text{Co(OH)F} + \text{O}_2 & \rightarrow 2\text{Co}_3\text{O}_4 + 6\text{HF} \\
\end{align*}
\]

In addition, the amount of NH₄F in the reaction system plays a crucial role in the mass loading of products on Ni foam. After thermal treatment, the mass loading of Co₃O₄ is approximately
0.95, 6.8, 6.3, and 3.96 mg cm\(^{-2}\) for 1 mmol, 5 mmol, 10 mmol, and 20 mmol of NH\(_4\)F, respectively. Although Co\(_{1.3}\)(OH)\(_{0.7}\) could reduce the nucleation rate and enhance the mass loading of products, a high amount of NH\(_4\)F (20 mmol) still suppresses further increase of the mass loading. Optical images of these samples are shown in Fig. S4 in ESI.† In Fig. S4-a,† the differences in the colours of the precursors are due to their different morphologies and chemical compositions.

From the above analysis, this work further reveals that F\(^-\) could slow down the nucleation rate during such a hydrothermal reaction process, which is in accordance with previous reports.\(^{23}\) Most importantly, it also elucidates a new growth mechanism: firstly, the amount of NH\(_4\)F in the solution system affects the chemical composition of the precursor. Secondly, with increasing amounts of NH\(_4\)F in the solution, the growth of products will tend towards the formation of more ordered states and more distinct hierarchical structures. Thirdly, with increasing amounts of NH\(_4\)F in the solution, the morphology of products will tend towards denser structures. Fourthly, the amount of NH\(_4\)F in the solution system will affect the mass loading of products.

5. Electrochemical analysis

Fig. 6a shows typical cyclic voltammetry (CV) curves for the Co\(_3\)O\(_4\)-1, Co\(_3\)O\(_4\)-2, Co\(_3\)O\(_4\)-3, and Co\(_3\)O\(_4\)-4 electrodes in the potential range of 0–0.55 V at the scan rate of 5 mV s\(^{-1}\). The CV curve shapes reveal the pseudocapacitive characteristics of the four Co\(_3\)O\(_4\) electrodes. There are two oxidation peaks, P\(_1\) and P\(_2\), which are located at 0.3–0.45 V for Co\(_3\)O\(_4\)-3 and Co\(_3\)O\(_4\)-4, while Co\(_3\)O\(_4\)-1 and Co\(_3\)O\(_4\)-2 only exhibit one oxidation peak. The two reduction peaks P\(_3\) and P\(_4\) are located at 0.3–0.4 V and 0.1–0.2 V for the four electrodes. The reduction peak P\(_3\) and oxidation peak P\(_1\) are related to the following redox reaction: Co\(_3\)O\(_4\) + H\(_2\)O + OH\(^-\) = 3CoOOH + e\(^-\), and the reduction peak P\(_2\) are associated with the following redox reaction: CoOOH + OH\(^-\) = CoO\(_2\) + H\(_2\)O + e\(^-\).\(^{19}\) In addition, the redox peaks of the four electrodes have different potential positions, which could be attributed to the different available sites for the different morphologies.\(^{24–27}\) Compared with the other electrodes, the Co\(_3\)O\(_4\)-2 electrode has the largest CV area, revealing the highest level of stored charge. The CV curves at various scan rates are shown in Fig. S5.† The CV curves of bare Ni foam and 6 M hydrochloric acid treated Ni foam are shown in Fig. S6,† and although Ni foam contributes some capacitance (about 9% for Co\(_3\)O\(_4\)-2 electrode) after 6 M hydrochloric acid treatment, most of the capacitance is from Co\(_3\)O\(_4\) material. The composition of 6 M hydrochloric acid treated Ni foam was investigated using XRD and XPS. In Fig. S7,† the peaks at 44.5°, 51.8° and 76.3° are ascribed to the (111), (200) and (220) planes of metallic nickel (JCPDS no. 04-0850), respectively, and no apparent other peaks are observed, which means the main composition is still the metallic nickel. In Fig. S8a,† the peaks at 856.5 and 874.2 eV are assigned to Ni 2p\(_{3/2}\) and Ni 2p\(_{1/2}\) of Ni\(^{2+}\), respectively, while in Fig. S8b,† the peak at 532.5 eV is ascribed to O 1s, indicating Ni–O–H at the surface.\(^{28}\)

Fig. 6b shows typical charge and discharge curves of the four samples at the current density of 5 mA cm\(^{-2}\) within the potential range of 0–0.45 V. It can be seen that all the curves have apparent voltage plateaus in the discharging process, indicating their pseudocapacitive behaviour, although the lengths of the discharging times and discharging plateaus are different. The differences in discharging plateaus for the four electrodes also could be ascribed to their different available sites for different morphologies. Among these discharging curves, the Co\(_3\)O\(_4\)-2 discharging time is the longest. From the discharging curves, the specific area capacitance can be calculated according to the following equation:

\[
C_{A} = I \times \Delta t / (\Delta V \times S)
\]

(8)

where \(C_{A}\) is the specific area capacitance (F cm\(^{-2}\)), \(I\) is the discharging current (A cm\(^{-2}\)), \(\Delta t\) is the discharging time (s), \(\Delta V\) is the discharging potential range (V), and \(S\) the area (cm\(^2\)), respectively.

The capacitance per unit area of Co\(_3\)O\(_4\)-1, Co\(_3\)O\(_4\)-2, Co\(_3\)O\(_4\)-3, and Co\(_3\)O\(_4\)-4 was 0.5, 1.92, 1.53, and 0.87 F cm\(^{-2}\), respectively. At the charge current density of 30 mA cm\(^{-2}\), respectively. The Co\(_3\)O\(_4\)-2 electrode displays the highest capacitance among them, which could be ascribed to its high mass loading and unique morphology.

Fig. 6c presents the specific area capacitance of the Co\(_3\)O\(_4\)-1, Co\(_3\)O\(_4\)-2, Co\(_3\)O\(_4\)-3, and Co\(_3\)O\(_4\)-4 electrodes at various current densities, from 5 mA cm\(^{-2}\) to 30 mA cm\(^{-2}\), respectively. At the current density of 30 mA cm\(^{-2}\), the specific area capacitance retention is 60.00%, 72.91%, 64.70%, and 60.91% for the Co\(_3\)O\(_4\)-1, Co\(_3\)O\(_4\)-2, Co\(_3\)O\(_4\)-3, and Co\(_3\)O\(_4\)-4 electrodes, respectively. Among all these electrodes, the Co\(_3\)O\(_4\)-2 electrode displays the best specific area capacitance retention, which is also superior to previous reported similar freestanding Co\(_3\)O\(_4\) material.\(^{29–31}\) The charge and discharge curves of the different electrodes at various current densities are shown in Fig. S9.†
In Fig. 6d, the cycling stability of Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 was tested at current density of 5 mA cm⁻² over 3000 cycles. After 3000 cycles, the capacitance retention was 100.00% (0.5 F cm⁻²), 150% (2.38 F cm⁻²), 107% (1.64 F cm⁻²), and 111% (0.97 F cm⁻²) for Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4, respectively, which reveals that Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 undergo a capacitance activation process during charge–discharge cycling. Compared with Co₃O₄-3 and Co₃O₄-4, there is an apparent trend towards increasing capacitance for Co₃O₄-2, which could be observed in the first 1150 cycles (from 1.92 F cm⁻² to 3.16 F cm⁻²), with the capacitive activation process during charging–discharging similar to that in most previous reports.⁹–¹⁴ The capacitance retention of Co₃O₄-2, based on its maximum value of 3.16 F cm⁻², still could amount to 91% after 3000 cycles.

According to many previous reports (Table S1†), free-standing Co₃O₄, NiCo₂O₄, or MnO₂ electrodes synthesized by hydrothermal reaction methods for supercapacitors usually exhibit low specific area capacitance (approximately 0.1–0.8 F cm⁻²), which severely obstructs their practical application. In order to further enhance their specific area capacitance, a second step reaction was adopted to make them into “core/shell” structures, and the specific area capacitance could then reach 0.5–2.5 F cm⁻².

In this work, we successfully demonstrate that NH₄F could effectively control the active material mass loading on Ni foam and its product morphology through a one-step hydrothermal reaction, thereby obtaining the optimized high specific area capacitance of the Co₃O₄-2 electrode (1.92 F cm⁻²), which is an ideal potential electrode with high specific area capacitance for practical application.

Fig. S10(a and b)† show the electrochemical impedance spectroscopy plots collected before cycling and after 3000 cycles for the Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 electrodes, respectively. Fig. S10c† is the equivalent circuit for determining the electrochemical impedance. The semicircle in the high frequency region reveals the properties of the electrode surface, indicating the charge transfer resistance (Rct). After 3000 cycles, the Rct of the Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 electrodes all decreased dramatically, which could be the reason for their capacitance activation during cycling.⁶ In addition, reaction of the Ni foam with the electrolyte during cycling may be another factor behind the capacitance increase.⁹ Fig. S11(a–d)† shows the Bode plots of the Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 electrodes, respectively, and their phase angles reached nearly −80 degree at 0.01 Hz, which represents their ideal capacitor nature.

6. Conclusions

In summary, four morphologies of Co₃O₄ on Ni foam (nanowires, thin nanowire-clusters, thick nanowire-clusters, and fan-like bulks) were obtained through conventional hydrothermal reaction with different amounts of NH₄F as an additive, which demonstrated its potential for tuning the morphology of nanoscale transition metal oxides. Through investigation of the morphological evolution process for the Co₃O₄ precursors in their different reaction stages, some novel growth mechanisms are proposed: (1) the amount of NH₄F in the solution system affects the chemical composition of the precursor; (2) with increasing amounts of NH₄F in the solution system, the morphology will tend towards more ordered states and more distinct hierarchical structures; (3) with increasing amounts of NH₄F in the solution system, the growth of the products will tend to form denser structures; (4) the amount of NH₄F in the solution system will affect the mass loading of products. The electrochemical performances of the four Co₃O₄ electrode materials for supercapacitors were tested, and the Co₃O₄ with thin-nanowire-cluster morphology exhibits the best electrochemical performance (specific capacitance of 1.92 F cm⁻² at the current density of 5 mA cm⁻², rising to 2.88 F cm⁻² after 3000 cycles, and rate capability of 72.91% at the current density of 30 mA cm⁻²), which makes it an ideal potential electrode material for practical application in supercapacitors.

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Notes and references