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Tuning the morphology of Co₃O₄ on Ni foam for supercapacitor application

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_3O_4 on Ni foam for supercapacitor application†

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In this work, NH_4F was used as a vital additive to control the morphology of Co_3O_4 precursors on Ni foam in a conventional hydrothermal reaction, and then, *via* thermal decomposition, to obtain Co_3O_4 material. The amount of NH_4F plays a pivotal role in the formed morphology of the Co_3O_4 precursors, and four morphologies of Co_3O_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_3O_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_4F in the solution system affects the chemical composition of the precursors; (2) with an increasing amount of NH_4F 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_4F in the solution system, the growth of products will tend to form denser structures; (4) the amount of NH_4F in the solution system will affect the mass loading of products. The four different morphologies of Co_3O_4 were tested as free-standing electrode materials for supercapacitor application. Co_3O_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} .

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1. Introduction

Spinel oxide Co_3O_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_3O_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_3O_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_3O_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 polyvinylidene difluoride (PVDF) binder. Among the many synthesis methods for Co_3O_4 , hydrothermal reaction could satisfy the above requirements, and it also could be suitable for large-scale production.²¹ The mass loading of Co_3O_4 on Ni foam through hydrothermal reaction is limited, however, which renders relatively low area capacitance. NH_4F 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_3O_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_4F were applied as an additive, and it

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was found that the NH_4F plays a pivotal role in forming the morphology of the Co_3O_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_3O_4 precursors was investigated according to their intermediates in different reaction stages, and some novel growth mechanisms are proposed: firstly, the amount of NH_4F applied in the solution system affects the chemical composition of the precursor. With a low amount of NH_4F , the precursor is $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$, while with medium and high amounts of NH_4F , the precursor is $\text{CoF}_{1.3}(\text{OH})_{0.7}$. Secondly, with increasing amounts of NH_4F 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_4F in the solution system, the final products tend to form denser structures. Nanowires tend to stack together with the medium amount of NH_4F , and the gaps among nanowires are reduced significantly compared with the sparsely distributed nanowires that are obtained with a small amount of NH_4F . With a high amount of NH_4F , the nanowires are replaced by nanosheets, which further promote a dense structure. Fourthly, the amount of NH_4F in the solution system affects the mass loading of products on the Ni foam substrate. On introducing a medium amount of NH_4F into the solution system, the mass loading on Ni foam will increase notably compared with that with a low amount of NH_4F , although the mass loading on Ni foam does not increase linearly as the amount of NH_4F increases, and a high amount of NH_4F suppresses further increases in the mass loading on Ni foam.

The electrochemical performances of the four different morphologies of Co_3O_4 as free-standing electrode materials were tested for supercapacitor application. Co_3O_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_3O_4 on Ni foam

All the chemical reagents were of analytical grade and were used without further purification. Ni foam ($1 \text{ cm} \times 3 \text{ cm}$) 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 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 10 mmol urea, and different amounts of NH_4F (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_3O_4 . The corresponding samples synthesised by adding 1 mmol, 5 mmol, 10 mmol, and 20 mmol NH_4F were denoted as Co_3O_4 -1, Co_3O_4 -2, Co_3O_4 -3, and Co_3O_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, $\lambda = 1.5406 \text{ \AA}$). 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_3O_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 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_3O_4 are shown in Fig. 1a–h. Fig. 1(a and b) shows the morphology of Co_3O_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_3O_4 -2, which is very different from the morphology of Co_3O_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_3O_4 -2, in Fig. 1(e and f), the morphology of Co_3O_4 -3 with Co_3O_4 -2, in Fig. 1(e and f), the morphology of Co_3O_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_3O_4 -1, Co_3O_4 -2, and Co_3O_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

Fig. 1 SEM images of the samples: Co_3O_4 -1 (a and b), Co_3O_4 -2 (c and d), Co_3O_4 -3 (e and f), and Co_3O_4 -4 (g and h).

noted that the nanowires of Co_3O_4 -2 and Co_3O_4 -3 on Ni foam are denser than those of Co_3O_4 -1. In Fig. 1(g and h), the morphology of Co_3O_4 -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 Co_3O_4 -3 and Co_3O_4 -4 have never been reported previously.

In Fig. 2, the XRD patterns reveal the crystal structure and phase purity of as-obtained Co_3O_4 -1, Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -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 Co_3O_4 (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 Co_3O_4 -1, Co_3O_4 -2, and Co_3O_4 -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

Fig. 2 XRD patterns of the Co_3O_4 samples on Ni foam.

Fig. 3 TEM images of Co_3O_4 -1 (a), Co_3O_4 -2 (c), Co_3O_4 -3 (e), and Co_3O_4 -4 (g); HRTEM images of Co_3O_4 -1 (b), Co_3O_4 -2 (d), Co_3O_4 -3 (f), and Co_3O_4 -4 (h).

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 Co_3O_4 -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 Co_3O_4 , 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 Co_3O_4 -1 (1 mmol NH_4F), Co_3O_4 -2 (5 mmol NH_4F), Co_3O_4 -3 (10 mmol NH_4F), and Co_3O_4 -4 (20 mmol NH_4F), for reaction times of 20 min, 1 h, 2 h, and 4 h. On introducing a low amount of NH_4F (1

Fig. 4 Pathways of morphology evolution shown in SEM images of the corresponding precursors of Co_3O_4 -1 (a–d), Co_3O_4 -2 (e–h), Co_3O_4 -3 (i–l), and Co_3O_4 -4 (m–p) for different reaction times: 20 min, 1 h, 2 h, and 4 h.

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 NH_4F (5 and 10 mmol) and a high amount of NH_4F (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 NH_4F were more ordered than those with 5 mmol of NH_4F . 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 NH_4F 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 NH_4F was still greater than

that with less NH_4F (5 mmol). After 4 h, the morphologies with medium amounts (5 and 10 mmol) of NH_4F evolved from bulks into nanowire-clusters (Fig. 4h and l), which reveals the reason why clusters with 10 mmol of NH_4F 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 NH_4F (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 NH_4F , 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 NH_4F (1 mmol) leads to a disordered state, while the growth of nanowire clusters with medium amounts of NH_4F (5 and 10 mmol) displays relatively ordered behaviour, although the growth of nanowire clusters with 10 mmol of NH_4F is more ordered than that of nanowire-clusters with 5 mmol of NH_4F , and the hierarchical structure becomes more distinct. It should

be noted that the bulks with the highest amount of NH_4F (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 NH_4F affects the morphology of the Co_3O_4 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 NH_4F (1 mmol) is $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$, while the precursors with medium amounts of NH_4F (5 and 10 mmol) and the highest amount of NH_4F (20 mmol) are $\text{CoF}_{1.3}(\text{OH})_{0.7}$, which could explain our observations that introducing medium amounts of NH_4F (5 and 10 mmol) or a high amount of NH_4F (20 mmol) makes the morphology evolution process more complicated. The composition of Co_3O_4 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 CO_3^{2-} 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 CO_3^{2-} , respectively.²² 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 Co^{2+} ions at the initial stage and then release the Co^{2+} ions slowly,²³ but from this work, when there are medium amounts of NH_4F (5 and 10 mmol) or a high amount of NH_4F (20 mmol) in the solution system, the precursor product is $\text{CoF}_{1.3}(\text{OH})_{0.7}$, which could explain the greater complication of the morphology evolution process. With a medium (5 or 10 mmol) or high (20 mmol) amount of NH_4F in the solution system, the F^- not only takes part in the reaction, but also forms the stable precursor product

$\text{CoF}_{1.3}(\text{OH})_{0.7}$. This also suggests that the formation of $\text{CoF}_{1.3}(\text{OH})_{0.7}$ helps to reduce the nucleation rate to some extent, making the morphologies with 5 and 10 mmol of NH_4F experience an evolution from bulks to nanowire clusters. It should be noted that 20 mmol of NH_4F 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 NH_4F on the morphology are proposed, as shown in Fig. 5. The hydrothermal chemical reaction could be suggested as follows:

Subsequently, the precursors are transformed to stable Co_3O_4 phase in air.

In addition, the amount of NH_4F in the reaction system plays a crucial role in the mass loading of products on Ni foam. After thermal treatment, the mass loading of Co_3O_4 is approximately

Fig. 5 Proposed corresponding mechanisms for the effect of NH_4F on morphology evolution.

0.95, 6.8, 6.3, and 3.96 mg cm⁻² for 1 mmol, 5 mmol, 10 mmol, and 20 mmol of NH₄F, respectively. Although CoF_{1.3}(OH)_{0.7} could reduce the nucleation rate and enhance the mass loading of products, a high amount of NH₄F (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 NH₄F in the solution system affects the chemical composition of the precursor. Secondly, with increasing amounts of NH₄F in the solution system, the growth of products will tend towards the formation of more ordered states and more distinct hierarchical structures. Thirdly, with increasing amounts of NH₄F in the solution, the morphology of products will tend towards denser structures. Fourthly, the amount of NH₄F in the solution system will affect the mass loading of products.

5. Electrochemical analysis

Fig. 6a shows typical cyclic voltammetry (CV) curves for the Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 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 Co₃O₄ electrodes. There are two oxidation peaks, P₁ and P₂, which are located at 0.3–0.45 V for Co₃O₄-3 and Co₃O₄-4, while Co₃O₄-1 and Co₃O₄-2 only exhibit one oxidation peak. The two reduction peaks P₃ and P₄ are located at 0.3–0.4 V and 0.1–0.2 V for the four electrodes. The reduction peak P₄ and oxidation peak P₁ are related to the following redox reaction: Co₃O₄ + H₂O

+ OH⁻ = 3CoOOH + e⁻, and the reduction peak P₃ and oxidation peak P₂ are associated with the following redox reaction: CoOOH + OH⁻ = CoO₂ + H₂O + e⁻.¹⁰ 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 Co₃O₄-2 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 Co₃O₄-2 electrode) after 6 M hydrochloric acid treatment, most of the capacitance is from Co₃O₄ 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 Ni²⁺, 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 Co₃O₄-2 discharging time is the longest. From the discharging curves, the specific area capacitance can be calculated according to the following equation:

$$C_A = I \times \Delta t / (\Delta V \times S) \quad (8)$$

where C_A is the specific area capacitance (F cm⁻²), I is the discharging current (A cm⁻²), Δt is the discharging time (s), ΔV is the discharging potential range (V), and S the area (cm²), respectively.

The capacitance per unit area of Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 was 0.5, 1.92, 1.53, and 0.87 F cm⁻², respectively. The Co₃O₄-2 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 Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 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 Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 electrodes, respectively. Among all these electrodes, the Co₃O₄-2 electrode displays the best specific area capacitance retention, which is also superior to previous reported similar freestanding Co₃O₄ material.^{29–31} The charge and discharge curves of the different electrodes at various current densities are shown in Fig. S9.†

Fig. 6 Electrochemical characterization of supercapacitors with Co₃O₄-1, Co₃O₄-2, Co₃O₄-3, and Co₃O₄-4 electrodes: CV curves at the scan rate of 5 mV s⁻¹ (a); charge and discharge curves at the current density of 5 mA cm⁻² (b); specific area capacitance at various current densities (c); cycling stability testing at 5 mA cm⁻² for 3000 cycles (d).

In Fig. 6d, the cycling stability of Co_3O_4 -1, Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -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% (2.88 F cm^{-2}), 107% (1.64 F cm^{-2}), and 111% (0.97 F cm^{-2}) for Co_3O_4 -1, Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -4, respectively, which reveals that Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -4 undergo a capacitance activation process during charge–discharge cycling. Compared with Co_3O_4 -3 and Co_3O_4 -4, there is an apparent trend towards increasing capacitance for Co_3O_4 -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.^{32–37} The capacitance retention of Co_3O_4 -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 Co_3O_4 , NiCo_2O_4 , or MnO_2 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 NH_4F 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 Co_3O_4 -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 Co_3O_4 -1, Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -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 (R_{ct}). After 3000 cycles, the R_{ct} of the Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -4 electrodes all decreased dramatically, which could be the reason for their capacitance activation during cycling.³⁸ In addition, reaction of the Ni foam with the electrolyte during cycling may be another factor behind the capacitance increase.²⁸ Fig. S11(a–d)† shows the Bode plots of the Co_3O_4 -1, Co_3O_4 -2, Co_3O_4 -3, and Co_3O_4 -4 electrodes, respectively, and their phase angles reached nearly -80 degree at 0.01 Hz , which represents their ideal capacitor nature.²⁸

6. Conclusions

In summary, four morphologies of Co_3O_4 on Ni foam (nanowires, thin nanowire-clusters, thick nanowire-clusters, and fan-like bulks) were obtained through conventional hydrothermal reaction with different amounts of NH_4F 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 Co_3O_4 precursors in

their different reaction stages, some novel growth mechanisms are proposed: (1) the amount of NH_4F in the solution system affects the chemical composition of the precursor; (2) with increasing amounts of NH_4F in the solution system, the morphology will tend towards more ordered states and more distinct hierarchical structures; (3) with increasing amounts of NH_4F in the solution system, the growth of the products will tend to form denser structures; (4) the amount of NH_4F in the solution system will affect the mass loading of products. The electrochemical performances of the four Co_3O_4 electrode materials for supercapacitors were tested, and the Co_3O_4 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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