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Ultrathin Co_3O_4 nanosheet arrays with high supercapacitive performance

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Constructing nanostructures with desirable morphology and size is a critical issue for pursuing high performance electrode materials. Ultrathin Co_3O_4 nanosheet arrays, which are composed of well aligned uniform long-range ($\sim 5 \mu\text{m}$ in length) and thin ($\sim 10 \text{ nm}$ in thickness) nanosheets, with reasonable mass loading on Ni foam are prepared by a two-step hydrothermal reaction. As a supercapacitor electrode, a superior specific capacitance ($\sim 1782 \text{ F g}^{-1}$) is obtained at current density of 1.8 A g^{-1} (5 mA cm^{-2}), much larger than that of the thicker nanostructures ($\sim 300 \text{ F g}^{-1}$). The ultrathin nanosheet arrays electrode exhibits good rate capabilities, maintaining 51% of the initial capacity at current density of 30 mA cm^{-2} , and excellent long-term stability, remaining $>90\%$ of capacitance after 2000 cycles. Such high performance is attributed to the desirable morphologies, uniform architecture and high surface area. The results manifest that ultrathin Co_3O_4 nanosheet arrays are promising electrode material for supercapacitor in future application.

Many alternative energy technologies have been developed in an attempt to alleviate the critical problems of escalating energy crisis and greenhouse gas pollution, derived from the consumption of fossil fuels^{1–4}. As an emerging advanced electrochemical energy storage form, supercapacitors (SCs) could offer higher power density, longer cycling life, shorter charge/discharge time, and better safety when compared with batteries⁵. SCs store energy on the basis of either charge accumulation (electric double layer capacitors, EDLC) or fast reversible Faradaic reactions (pseudocapacitors) on the surface. For the purpose of improving SCs' energy densities, numerous efforts have been made to investigate pseudocapacitive transition metal oxides or hydroxide (such as RuO_2 ⁶, MnO_2 ⁷, NiO ⁸, Co_3O_4 ⁹, $\text{Ni}(\text{OH})_2$ ¹⁰, $\text{Co}(\text{OH})_2$ ¹¹, NiCo_2O_4 ¹² etc.) and their composites with conductive additives^{13–16}, which could produce higher specific capacitance than typical carbonaceous materials with electric double layer capacitance^{17–19}. For example, Hu etc. has reported that NiCo_2O_4 aerogel exhibited better electrical conductivity and higher electrochemical activity (1400 F g^{-1}) than pure NiO and Co_3O_4 ²⁰. We have also developed NiO and $\text{Ni}(\text{OH})_2$ nanoarrays electrodes with high specific capacitance of 2018 F g^{-1} and 2675 F g^{-1} , respectively^{10,21}. Among these available pseudocapacitive materials, Co_3O_4 is particularly attractive for application in SCs, due to its low cost, low environmental footprint, great redox activity and especially, extremely high theoretical specific capacitance (ca. 3560 F g^{-1})^{22,23}. However, the observed specific capacitance for Co_3O_4 are much lower than its theoretical value²⁴, and it is still challenging and imperative to improve its specific capacitance as well as rate capability and long term stability with rational design and fabrication process.

Construction of nanostructure with desirable morphology and size is of great importance for addressing this issue. Long-range (micrometer in length) and thin (nanometer in thickness) structures have been regarded as promising morphologies in the field of energy storage²⁵. Generally, the long-range structure can lower the internal resistance, facilitate the electron transfer rate as compared with the noncontinuous oxide framework composed of nanoparticles²⁶, and the thin thickness can preserve the advantages of nanosized materials, such as the short ion diffusion path and the large surface area, which is also an essential fact for both electrochemical double layer capacitance and pseudo-capacitance. Considering that the concentration polarization is an obstacle for long-range structures, a suitable porosity would also play an important role in easing the mass transfer of electrolyte^{5,27}. Three dimensional (3D) mesoporous architectures by having two dimensional (2D) ultrathin nanosheets grown in a vertical fashion on a conductive substrate will meet all these requirements for the improvement of electrochemical performance of the materials. Besides, nanoarray architectures could prevent agglomeration and ensure that large proportion of nanocrystals participate in the electrochemical reaction. As well, the open space among neighboring nanosheets allows fast redox reactions, and thus, improves the charge-discharge rate²⁸. In this regards, researchers have fabricated nanosheet-like arrays for electrochemical applications. For example, CoOOH nanosheet film on the nickel foam prepared by chemical bath deposition method have been demonstrated to show high rate capacitance²⁹. Very recently, Lou et al. also reported the ultrathin mesoporous Co_3O_4

Figure 1 | Schematic illustration of the synthesis process of ultrathin Co_3O_4 nanosheet arrays.

nanosheet arrays³⁰ and mesoporous NiCo_2O_4 nanosheets on conductive substrates¹² by electrochemical or hydrothermal method with high performance for electrochemical capacitors. But the relatively low mass loading of active materials on those electrodes limited their practical application.

In this work, ultrathin Co_3O_4 nanosheet arrays with reasonable mass loading were developed by a two-step hydrothermal reaction and following calcination process. The ultrathin Co_3O_4 nanosheet arrays were composed of well aligned uniform long-range ($\sim 5 \mu\text{m}$ in length) and thin ($\sim 10 \text{ nm}$ in thickness) nanosheets, fitting the desirable structure principles as mentioned above. As expected, they exhibited superior pseudo-capacitance (1782 F g^{-1}), much larger than relatively thick nanostructures (354 F g^{-1}). Additionally, the samples performed well at high current density and the capacitances remain $>90\%$ after 2000 cycles, indicating its high rate capability and excellent cycling life. These results manifest that our samples are promising for future practical application and also provide a deeper understanding of the thickness effect on the supercapacitive performance.

Results

Synthesis of Co_3O_4 nanoarrays. The synthesis of Co_3O_4 nanosheet arrays is illustrated in Fig. 1. Hexagonal $\beta\text{-Co}(\text{OH})_2$ nanosheet arrays were firstly grown directly on nickel foam substrate via a facile hydrothermal process³¹. Then, thinner nanosheet arrays with different morphology and size were obtained by a secondary hydrothermal reaction of treating the as-prepared $\beta\text{-Co}(\text{OH})_2$ samples with additional Co^{2+} salt and appropriate bases (e.g. urea or hexamethylenetetramine (HMT)) through a process involving the dissolution and recrystallization of hexagonal nanosheet arrays. After that, the targeted Co_3O_4 nanoarrays were obtained by a simple calcination treatment (the obtained Co_3O_4 nanosheet arrays synthesized by urea and HMT were denoted as NS-U and NS-H, respectively). Thick Co_3O_4 nanosheet arrays were also prepared by directly calcinating $\beta\text{-Co}(\text{OH})_2$ nanosheet arrays for comparison (denoted as NS). Typical SEM images in Fig. 2 and Fig. S1 clearly show the morphologies of the products. The $\beta\text{-Co}(\text{OH})_2$ nanosheet arrays exhibited dense and compact films consisted of many thick hexagonal nanosheets, which grew vertically and cross-linked on Ni substrate (Fig. S1). The calcination of the nanoarray did not change its size and morphology (Fig. 2a and b). The average thickness and length of an individual sheet in NS were about 200 nm and $4 \mu\text{m}$, respectively. After the secondary hydrothermal reaction of $\beta\text{-Co}(\text{OH})_2$ arrays with additional Co^{2+} salt and appropriate bases, the samples kept the 3D mesoporous architectures well, but it is interesting that the thickness of the nanosheets sharply decreased and the morphology simultaneously changed. When we used urea as base source, the resulted nanosheet was rectangular with the size of 40 nm in thickness, $1 \mu\text{m}$ in width and $5 \mu\text{m}$ in length (NS-U, Fig. 2d and e). Furthermore, ultrathin nanosheets with the thickness decreased to about 10 nm were obtained, when we chose HMT as base source

(NS-H, Fig. 2g and h). The decreased thickness of the 3D nanoarray architecture usually means higher specific surface area and more efficient use of the active materials, and thus, greater improvements in the performance of an electro-active material were expected. Besides, the low magnification and cross-section SEM images in Fig. S2a–c give a full view of the structure of the electrode, indicating that the Co_3O_4 nanoarrays distribute uniformly on the Ni foam and have a tight connection with the substrate. EDS results in Fig. S2d show that there are only Co and O element existing in the nanoarrays (the other peaks occurring in the pattern are due to the SEM Pt spraying process), and no Ni element could be detected in, confirming the stability of the Ni foam during the hydrothermal and annealing process.

To further investigate the crystal structure, the samples were subjected to XRD measurement. As shown in Fig. 3 and Fig. S1, the diffraction peaks of all three samples NS, NS-U and NS-H could be indexed as pure spinel phased Co_3O_4 with a lattice constant of $a = 0.8084 \text{ nm}$ (JCPDF: 42-1467) and the ones of $\beta\text{-Co}(\text{OH})_2$ nanosheet arrays were almost in accordance to its standard pattern (JCPDF: 30-0443) as we previously reported³¹ (the peaks marked “#” stand for the Ni substrate). HRTEM analysis was also performed on the nanoarrays. Two lattice spaces of 0.23 nm and 0.29 nm were observed, which correspond to the $(2\bar{2}2)$ and (220) planes of Co_3O_4 , indicating that $(1\bar{1}\bar{2})$ was the dominant exposed plane of all the Co_3O_4 nanoar-

Figure 2 | SEM and HRTEM images of Co_3O_4 nanoarrays. (a–c) NS; (d–f) NS-U; (g–i) NS-H.

Figure 3 | XRD patterns of (a) NS, (b) NS-U and (c) NS-H, as well as the standard pattern of Co₃O₄ (JCPDF: 42-1467) (the peaks marked “#” stand for the Ni substrate).

rays (Fig. 2c, f and i). The HRTEM images (Fig. S3a–c) also demonstrated that each ultrathin Co₃O₄ nanosheet consisted of numerous interconnected nanoparticles forming a mesoporous structure and it possessed inter-particle mesopores with a size ca. 2 nm in the nanosheets. From the N₂ adsorption-desorption isotherm results (Fig. S3d–f), the average pore size of the NS, NS-U and NS-H were 4.86 nm, 6.80 nm and 7.65 nm, respectively. The mesoporous structure gave rise to a relatively high Brunauer-Emmett-Teller (BET) specific surface area (95 m² g^{−1} for NS, 143 m² g^{−1} for NS-U and 211 m² g^{−1} for NS-H).

Morphology evolution mechanism. In order to have a closer inspection of the morphology evolution processes of NS-U and NS-H, samples at different reaction stages were collected. The secondary hydrothermal reaction process can be considered as a coordinating etching and recrystallization process for the nanosheets. During this process, excess urea or HMT introduced to the solution system can coordinating etch Co(OH)₂ by forming a soluble complex, along with the releasing of OH[−] to facilitate the recrystallization of Co(OH)₂. Fig. 4a–d show the SEM images of the NS-U obtained at various growth times, indicating the morphological and structural transformation from thick nanosheet to thin nanosheet array.

Clearly, the thick nanosheets were broken and some holes appeared in the bottom along with the dissolution of the nanosheets after the initial 3 h reaction. When the reaction time was further prolonged to 6 h and 9 h, the nanowires and nanobelts were successively grown out by replacing the thick nanosheets. Similarly, as shown in Fig. 4e–h, in the evolution process of NS-H, the surface of the thick nanosheets firstly became rough, which was corresponding to the coordinating etching of the thick nanosheet. With the reaction time increased to 6 h and 9 h, the nanosheets became thinner and looser. Finally, the ultrathin nanosheets arrays with thickness of about 10 nm were obtained after 12 h.

Electrochemical analysis. The electrochemical properties of the as-prepared NS-U and NS-H were measured in a three electrodes cell system (Fig. 5). NS was also tested as a control. Fig. 5a shows the typical cyclic voltammetry (CV) curves of the NS, NS-U and NS-H in the potential range of 0 V–0.6 V at the scan rate of 5 mV s^{−1}. Two redox peaks were clearly observed for the three samples, which correspond to the Co₃O₄/CoOOH/CoO₂ transformation associated with OH[−] anions (As we investigated previously, the Ni foam showed negligible contribution to the total capacitance²¹). The redox peaks of CV curves of NS-U and NS-H increased gradually with the decrease of the thickness of the sheets in nanoarrays when compared with the ones of NS, indicating more active materials were involved in the reaction. Furthermore, it is found interestingly that the shape of redox peaks of NS-H are much different from the ones of NS-U. A more narrow peak can be seen, which means a faster redox reaction of NS-H. Fig. 5b shows the typical charge and discharge curves of the three samples at the current density of 10 mA cm^{−2} (at a voltage window of 0 ~ 0.45 V). The symmetric triangular shape with more well-defined plateaus during the charge/discharge processes for NS-H suggests its better supercapacitive behaviors. The specific capacitance of the Co₃O₄ nanoarrays can be calculated based on the charge-discharge curves and the results at various current densities are presented in Fig. 5c. The NS, NS-U and NS-H exhibited successively increasing capacitances from 354 F g^{−1} (2.29 F cm^{−2}) to 1081 F g^{−1} (3.48 F cm^{−2}) and 1782 F g^{−1} (4.9 F cm^{−2}) at the current density of 5 mA cm^{−2}. Among them, the increased capacitances of NS-H (1782 F g^{−1}) are higher than most of previous reports (Table S1)^{32,33}. At the high current density of 30 mA cm^{−2}, the NS-U and NS-H still showed capacitances of 584 F g^{−1} (1.88 F cm^{−2}) and 913 F g^{−1} (2.51 F cm^{−2}), maintaining 54% and 51% of the capacitances. The good rate capability of the

Figure 4 | SEM images of the products at various reaction stages by setting the reaction time to NS-U: (a) 3 h, (b) 6 h, (c) 9 h, and (d) 12 h and NS-H: (e) 3 h, (f) 6 h, (g) 9 h, and (h) 12 h.

Figure 5 | Electrochemical characterizations of the NS, NS-U and NS-H. (a) CV curves at the scan rate of 5 mV s⁻¹; (b) galvanostatic charge/discharge curves at the current density of 10 mA cm⁻²; (c) average specific capacitance versus charge and discharge current density; (d) plots of average specific capacitance versus cycle numbers at a galvanostatic charge and discharge current density of 30 mA cm⁻².

NS-H was also confirmed by CV curves at relatively high scan rates up to 120 mV s⁻¹ as shown in Fig. S4. Besides, cycling performance in high-rate is another key factor in determining the supercapacitor electrodes for many practical applications. So in this case, we employed the cycle charge/discharge testing to examine the stability of the NS, NS-U and NS-H electrode at a high current density of 30 mA cm⁻² (see in Fig. 5d). A slight decrease (<10%) was observed in first 200 cycles and the negligible reduction occurred in the following 1800 cycles. We attributed the slight decay of the cycle stability of the NS-U and NS-H to the decreased thickness and stability of the Co₃O₄ nanostructures after the secondary hydrothermal reaction process. As a whole, the specific capacity kept at least 90% of the initial capacitance after 2000 cycles. The high stability indicates that the charge and discharge processes did not induce significant structural change of the electrodes as expected for pseudo-capacitance reactions. Combining the enhanced capacitance, remarkable rate capability and excellent cycle stability, we can conclude that ultrathin Co₃O₄ nanosheet arrays are advanced electrodes for supercapacitor and the strategy of constructing the unique architecture with high porosity, long range and thin thickness is efficient.

To access the feasibility of such ultrathin nanosheets array electrode, an asymmetric supercapacitor device were demonstrated by using NS-H as a positive electrode material and activated carbon (AC) as the negative electrode^{34–36}. The CV curves of the NS-H/AC asymmetric supercapacitor at the optimized mass ratio of NS-H/AC (AC: ~10 mg cm⁻²) in a upper potential limits (i.e., cell voltages) of 1.6 V at the scan rates from 5 mV s⁻¹ to 100 mV s⁻¹ were shown in Fig. 6a. The positive sweeps were symmetric to their corresponding negative sweeps for all CV curves, indicating the promising application to the asymmetric supercapacitor. To further evaluate the electrochemical performance of the asymmetric cell, galvanostatic charge/discharge tests within a voltage range of 0 V–1.6 V were performed. As seen in Fig. 6b, all of the charge/discharge curves generally show typical symmetric triangle shape curves, indicating

well balanced charge storage. The specific capacitances of the NS-H/AC of the total weight of the active material for both electrodes at 5 mA cm⁻², 10 mA cm⁻², 20 mA cm⁻², 30 mA cm⁻², 50 mA cm⁻², and 80 mA cm⁻² were 108 F g⁻¹, 96 F g⁻¹, 84 F g⁻¹, 73 F g⁻¹, 63 F g⁻¹, and 50 F g⁻¹, respectively. The good rate capability (68% capacitance retention from 5 mA cm⁻² to 30 mA cm⁻²) suggested the ability of this system to deliver the high power. The Ragone plot relating real power density to energy density of the NS-H/AC asymmetric supercapacitor was demonstrated in Fig. S5a, and the energy density of the asymmetric supercapacitor decreased from 134 Wh kg⁻¹ to 77 Wh kg⁻¹ when the current density increased from 5 mA cm⁻² to 30 mA cm⁻², exhibiting a high energy density of 134 Wh kg⁻¹ at a high power density of 1111 W kg⁻¹ at 5 mA cm⁻². In addition, the cycling performance of this asymmetric supercapacitor device was also measured in a high current density (30 mA cm⁻²). As shown in Fig. 5b, NS-H/AC asymmetric supercapacitor could keep ca. 80% of the initial capacitance after 800 cycles. These superior capacitive performances, including good electrochemical reversibility, excellent rate capability, and high stability, indicate the suitability of our sample for the asymmetric supercapacitor application.

Discussion

These high performances (including high specific capacity, better rate capability, and excellent stability) of the ultrathin Co₃O₄ nanosheets arrays are mainly attributed to the oriented 3D architecture of 2D long range (~5 μm in length) and thin (~10 nm in thickness) nanosheet arrays. First of all, the 2D nanosheet on conductive substrate reduces the internal resistance and the long range morphologies provides a continued pathway for charge transfer, which makes the redox reaction rate faster. To further elucidate the origin of high electrochemical performance, electrochemical impedance spectrum (EIS) was carried out to examine the NS, NS-U and NS-H electrode as shown in Fig. 7. The tested frequency region of EIS was from 10⁵ to 0.01 Hz and the voltage was set at 0.3 V vs.

Figure 6 | (a) CV curves of the asymmetric supercapacitor with a positive electrode of NS-H and a negative electrode of activated carbon (AC) at the scan rates from 5 mV s^{-1} to 100 mV s^{-1} ; (b) galvanostatic charge and discharge curves of the NS-H/AC asymmetric supercapacitor within a cell voltage of 0 V–1.6 V at current densities varying from 5 mA cm^{-2} to 80 mA cm^{-2} .

SCE. According to the quasi-vertical lines leaning to imaginary axis at the low frequency region (all the curves had a similar angle of $\sim 60^\circ$ with the real axis which was larger than typical Warburg angle of 45°), these three samples exhibited low Warburg impedance, indicating the facile electrolyte diffusion to the surface of the electrode¹¹. However, in the region of high frequency, NS-U and NS-H showed much smaller semicircles than NS. It is well known that the diameter of the semicircle in EIS spectrum could represent the electron transfer resistance (R_{ct}), which controls the electron transfer kinetics of the redox reaction at the electrode interface. Thus, both the NS-U and NS-H with long range nanosheet exhibited high electrochemical performance with low R_{ct} . The curve of NS-H showed a smaller diameter of the semicircle than that of the NS-U, and the intersection value of the real axis of NS-H was only $1.45 \Omega \text{ cm}^{-2}$ whereas that of the NS-U electrode was a little higher. Therefore, both the NS-U and NS-H showed good capacitive behavior but with a little difference. Above results demonstrate that a fast charge transfer process and a low internal resistance could be achieved by construction of nanoarray architecture with long range but thin morphology, and the NS-H with ultrathin structure performed better performance than NS-U.

Secondly, the thin thickness ($<50 \text{ nm}$ for NS-U and $<10 \text{ nm}$ for NS-H) increased the specific surface area of the nanosheet arrays, which resulted in the improvement of the contact area between electrode and electrolyte and facilitated the diffusion of electrolyte ion to the material, leading to more efficient utilization of the active material. Since the electrolyte had a penetration depth of approximately

20 nm^6 , it is reasonable that ultrathin NS-H was the most utilized and exhibited the highest specific capacitance. In order to verify the close relationship between the capacitance and the specific surface area, the electrochemical surface area (roughness factor) of all of the Co_3O_4 nanoarrays were measured. Fig. S6a–c shows the representative CV of the NS, NS-U and NS-H electrodes at different scan rates in a potential region of 0.125 V–0.175 V, which exhibits similar typical rectangular feature of an electrical double layer capacitor³⁷. In this potential region, charge transfer electrode reactions were considered to be negligible and the current was solely from electrical double layer charging and discharging. The plot of current against potential scan rate has a linear relationship (Fig. S6d) and its slope was the double layer capacitance ($i = C (\text{dE}/\text{dt})$). The areal surface area was calculated by dividing the electrode capacitance (F cm^{-2}) with the capacitance of smooth surface of Co_3O_4 ($60 \mu\text{F cm}^{-2}$)³⁷. The values of specific surface area of the NS, NS-U and NS-H were 98, 220 and $302 \text{ m}^2 \text{ g}^{-1}$, respectively, which were consistent with the BET results (Fig. S3). These results indicate that the thickness of the nanosheets which determines the specific surface area of array electrode is important for high electrochemical activity. All the results about the three samples are summarized in Table 1. In brief, with the decrease of thickness, the surface area of the nanosheet arrays increased correspondingly, which enlarged the electric double layer capacitance (180 F g^{-1} for NS-H). At the same time, ultrathin morphology also reduced the diffusion distance, maximized the active surface area for insertion and extrusion of OH^- , and consequently enhanced the pseudocapacitance (1602 F g^{-1} for NS-H)³⁸. Therefore, the high capacitance (1782 F g^{-1}) was achieved by simultaneously improving the electric double layer capacitance and pseudocapacitance. In addition, well-aligned nanoarray architecture could prevent agglomeration of active materials of the electrodes and also offer a tight binding between the material and the substrate. Hence, the capacitive performance could be improved significantly when compared with powdery materials³⁹.

In summary, we presented a new route for the synthesis of ultrathin Co_3O_4 nanosheet arrays on Ni foam substrate. The novel strategy was composed of a direct hydrothermal deposition of vertically aligned nanosheet-array precursors on Ni foam substrate, a secondary hydrothermal reaction and a subsequent calcination treatment. The obtained Co_3O_4 nanoarrays showed greatly enhanced capacitance (ca. from 354 F g^{-1} to 1782 F g^{-1}), together with excellent rate capability and high stability, which were attributed to the suitable long range and thin structure, uniform and oriented architecture and high electrochemical surface area. An asymmetric supercapacitor device based on Co_3O_4 NS-H/AC shows a high specific capacitance and specific energy (108 F g^{-1} and 134 Wh kg^{-1} within the potential

Figure 7 | Impedance plot of the NS, NS-U and NS-H measured at 0.3 V in low frequency region (insert is impedance plot of NS-U and NS-H in high frequency region).

Table 1 | Comparison of several calculated results of the NS, NS-U and NS-H. (The capacitance was calculated under the current density of 5 mA cm⁻²).

Material	Loading mass (mg cm ⁻²)	Thickness (~nm)	Surface area (m ² g ⁻¹)	BET (m ² g ⁻¹)	EDLC (F g ⁻¹)	Pseudo-capacitance (F g ⁻¹)	Specific capacitance (F g ⁻¹)	Areal capacitance (F cm ⁻²)
NS	6.46	200	98	95	58	296	354	2.29
NS-U	3.22	40	220	143	132	949	1081	3.48
NS-H	2.75	10	302	211	180	1602	1782	4.9

range of 0 V–1.6 V), indicating this kind of electrodes is very promising for future supercapacitor or other energy storage applications.

Methods

Synthesis. All of the chemicals were of analytical grade and used without any further purification. β -Co(OH)₂ nanosheet arrays were prepared according to our previous work³¹. Briefly, a piece of nickel foam (approximately 2 cm × 3 cm) was cleaned by concentrated HCl solution, ethanol and DI water with assistance of ultrasonication for several minutes. Afterward, the purified Ni foam was put against the wall of a Teflon lined stainless steel autoclave which contained a homogeneous solution of Co(NO₃)₂·6H₂O (2 mmol), NH₄F (8 mmol), CO(NH₂)₂ (10 mmol) and 36 ml distilled water. Then the autoclave was sealed and maintained at 100 °C for 6 h to synthesize the β -Co(OH)₂ nanosheet arrays. After a further calcination at 250 °C for 3 h, hexagonal Co₃O₄ nanosheet arrays (NS) were obtained. To synthesize ultrathin Co₃O₄ sheet arrays, a secondary hydrothermal reaction was adopted. Typically, the obtained β -Co(OH)₂ nanosheet arrays were put into the solution containing 1 mmol Co(NO₃)₂·6H₂O, 10 mmol urea (or 2 mmol Co(NO₃)₂·6H₂O and 4 mmol HMT (hexamethylenetetramine)) and 36 ml distilled water in autoclaves, and maintained at 120 °C for 12 h. After the hydrothermal reactions, the thin films on the metal substrate were taken out and rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80 °C for 6 h. Then the as-prepared products were calcinated at 250 °C for 3 h. The obtained Co₃O₄ nanosheet arrays synthesized by urea and HMT were denoted as NS-U and NS-H, respectively.

Characterizations. The size and morphology of the samples were characterized using a field-emission scanning electron microscope (SEM, Zeiss SUPRA 55) operating at 20 kV. High-resolution transmission electron microscopy (HRTEM) measurements were carried out using a JEOL JEM 2100 system operating at 200 kV. The phase purity and crystal structure of the three Co₃O₄ nanoarrays were examined by X-ray diffraction (XRD, Rigaku D/max 2500) at a scan rate of 10°/min in the 2 θ range from 15° to 90°. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area of samples by N₂ adsorption-desorption measurement on ASAP Tri-star II 3020. The pore size distributions (PSD) were derived from the desorption branch of the isotherm with the Barrett–Joyner–Halenda (BJH) method.

Electrochemical measurements. The electrochemical performances of the samples were evaluated on CHI 660D for cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) tests. 1 cm² of the nanoarrays film (without any polymer binder or conductive additives) was used for electrochemical measurements in a three-electrode beaker cell. A platinum electrode (1 cm²) and a saturated calomel electrode were used as counter and reference electrodes, respectively. Freshly prepared KOH aqueous solution at a concentration of 2 mol L⁻¹ was used as the electrolyte. An electrochemical activation step was performed for all the working electrodes before data were collected (50-cycle activation at 100 mV s⁻¹)⁴⁰. The mass loading of the active materials was obtained by calculating the increased mass on the Ni foam substrate. Typically, we firstly exactly tailored 6 cm² (3 cm × 2 cm) Ni foam and weighted it as m₁ mg. Then after twice hydrothermal reactions, the Ni foam was uniformly covered with red color and weighted as m₂ mg. Finally, after calcination treatment, the red film was converted to black color and the final sample was weighted as m₃ mg. The mass loading of the active materials was calculated as $m = (m_3 - m_1)/6$ mg cm⁻². The specific capacitance of Co₃O₄ nanoarrays grown on Ni foam was calculated from the CP curves based the following equation: $C = I\Delta t/(m\Delta V)$, where C, I, t, m and ΔV are the SC (F g⁻¹), the discharging current density (mA cm⁻²), the discharging time (s), loading mass (mg cm⁻²) and the discharging potential range (V), respectively.

- Arico, A. S. *et al.* Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* **4**, 366–377 (2005).
- Chan, C. K. *et al.* High-performance lithium battery anodes using silicon nanowires. *Nature Nanotech.* **3**, 31–35 (2008).
- Liu, N., Huo, K. F., McDowell, M. T., Zhao, J. & Cui, Y. Rice husks as a sustainable source of nanostructured silicon for high performance Li-ion battery anodes. *Sci. Rep.* **3**, 1919; DOI:10.1038/srep01919 (2013).
- Yang, N. *et al.* Two-dimensional graphene bridges enhanced photoinduced charge transport in dye-sensitized solar cells. *ACS Nano* **4**, 887–894.
- Simon, P. & Gogotsi, Y. Materials for electrochemical capacitors. *Nat. Mater.* **7**, 845–854 (2008).
- Hu, C.-C., Chang, K.-H., Lin, M.-C. & Wu, Y.-T. Design and tailoring of the nanotubular arrayed architecture of hydrous RuO₂ for next generation supercapacitors. *Nano Lett.* **6**, 2690–2695 (2006).
- Shi, S. *et al.* Flexible asymmetric supercapacitors based on ultrathin two-dimensional nanosheets with outstanding electrochemical performance and aesthetic property. *Sci. Rep.* **3**, 2598; DOI:10.1038/srep02598 (2013).
- Yuan, C. *et al.* Facile growth of hexagonal NiO nanoplatelet arrays assembled by mesoporous nanosheets on Ni foam towards high-performance electrochemical capacitors. *Electrochim. Acta* **78**, 532–538 (2012).
- Xiong, S. *et al.* Controllable Synthesis of Mesoporous Co₃O₄ Nanostructures with Tunable Morphology for Application in Supercapacitors. *Chem. Eur. J.* **15**, 5320–5326 (2009).
- Lu, Z., Chang, Z., Zhu, W. & Sun, X. Beta-phased Ni(OH)₂ nanowall film with reversible capacitance higher than theoretical Faradic capacitance. *Chem. Commun.* **47**, 9651–9653 (2011).
- Wang, L. *et al.* Layered α -Co(OH)₂ Nanocones as Electrode Materials for Pseudocapacitors: Understanding the Effect of Interlayer Space on Electrochemical Activity. *Adv. Funct. Mater.* **23**, 2758–2764 (2013).
- Zhang, G. & Lou, X. W. D. General Solution Growth of Mesoporous NiCo₂O₄ Nanosheets on Various Conductive Substrates as High-Performance Electrodes for Supercapacitors. *Adv. Mater.* **25**, 976–979 (2013).
- Xia, X. *et al.* Porous Hydroxide Nanosheets on Preformed Nanowires by Electrodeposition: Branched Nanoarrays for Electrochemical Energy Storage. *Chem. Mater.* **24**, 3793–3799 (2012).
- Yu, G. *et al.* Hybrid nanostructured materials for high-performance electrochemical capacitors. *Nano Energy* **2**, 213–234 (2013).
- Tang, Z., Tang, C. h. & Gong, H. A High Energy Density Asymmetric Supercapacitor from Nano-architected Ni(OH)₂/Carbon Nanotube Electrodes. *Adv. Funct. Mater.* **22**, 1272–1278 (2012).
- Zhang, G. Q. & Lou, X. W. D. Controlled Growth of NiCo₂O₄ Nanorods and Ultrathin Nanosheets on Carbon Nanofibers for High-performance Supercapacitors. *Sci. Rep.* **3**, 1470; DOI:10.1038/srep01470 (2013).
- Pandolfo, A. G. & Hollenkamp, A. F. Carbon properties and their role in supercapacitors. *J. Power Sources* **157**, 11–27 (2006).
- Yang, Q. *et al.* Metal oxide and hydroxide nanoarrays: Hydrothermal synthesis and applications as supercapacitors and nanocatalysts. *Prog. Nat. Sci.: Mater. Int.* **23**, 351–366 (2013).
- Wu, H., Pang, H. & Lou, X. W. D. Facile synthesis of mesoporous Ni_{0.3}Co_{2.7}O₄ hierarchical structures for high-performance supercapacitors. *Energy Environ. Sci.* **6**, 3619–3626 (2013).
- Wei, T. Y. *et al.* A Cost-Effective Supercapacitor Material of Ultrahigh Specific Capacitance: Spinel Nickel Cobaltite Aerogels from an Epoxide-Driven Sol-Gel Process. *Adv. Mater.* **22**, 347–351 (2010).
- Lu, Z., Chang, Z., Liu, J. & Sun, X. Stable ultrahigh specific capacitance of NiO nanorod arrays. *Nano Res.* **4**, 658–665 (2011).
- Cheng, H. *et al.* A facile method to improve the high rate capability of Co₃O₄ nanowire array electrodes. *Nano Res.* **3**, 895–901 (2010).
- Wei, T.-Y. *et al.* Cobalt oxide aerogels of ideal supercapacitive properties prepared with an epoxide synthetic route. *Chem. Mater.* **21**, 3228–3233 (2009).
- Xu, J. *et al.* Preparation and electrochemical capacitance of cobalt oxide (Co₃O₄) nanotubes as supercapacitor material. *Electrochim. Acta* **56**, 732–736 (2010).
- Meher, S. K. & Rao, G. R. Ultralayered Co₃O₄ for High-Performance Supercapacitor Applications. *J. Phys. Chem. C* **115**, 15646–15654 (2011).
- Hsu, Y.-K. *et al.* Reversible phase transformation of MnO₂ nanosheets in an electrochemical capacitor investigated by in situ Raman spectroscopy. *Chem. Commun.* **47**, 1252–1254 (2011).
- Zhou, H., Li, D., Hibino, M. & Honma, I. A Self-Ordered, Crystalline-Glass, Mesoporous Nanocomposite for Use as a Lithium-Based Storage Device with Both High Power and High Energy Densities. *Angew. Chem. Int. Ed.* **44**, 797–802 (2004).
- Li, Y., Tan, B. & Wu, Y. Mesoporous Co₃O₄ nanowire arrays for lithium ion batteries with high capacity and rate capability. *Nano Lett.* **8**, 265–270 (2008).
- Hosono, E. *et al.* Synthesis of the CoOOH fine nanoflake film with the high rate capacitance property. *J. Power Sources* **158**, 779–783 (2006).
- Yuan, C. *et al.* Growth of ultrathin mesoporous Co₃O₄ nanosheet arrays on Ni foam for high-performance electrochemical capacitors. *Energy Environ. Sci.* **5**, 7883–7887 (2012).
- Yang, Q. *et al.* Hierarchical Co₃O₄ nanosheet@nanowire arrays with enhanced pseudocapacitive performance. *RSC Adv.* **2**, 1663–1668 (2012).

32. Xia, X.-H. *et al.* Self-supported hydrothermal synthesized hollow Co_3O_4 nanowire arrays with high supercapacitor capacitance. *J. Mater. Chem.* **21**, 9319–9325 (2011).
33. Wang, H. *et al.* Supercapacitive properties of hydrothermally synthesized Co_3O_4 nanostructures. *J. Phys. Chem. C* **115**, 17599–17605 (2011).
34. Hsu, H.-Y. *et al.* Synthesis and characterization of mesoporous Ni-Co oxy-hydroxides for pseudocapacitor application. *Electrochim. Acta.* **94**, 104–112 (2013).
35. Kong, L.-B. *et al.* Asymmetric supercapacitor based on loose-packed cobalt hydroxide nanoflake materials and activated carbon. *J. Electrochem. Soc.* **156**, A1000–A1004 (2009).
36. Hu, C.-C., Chen, J.-C. & Chang, K.-H. Cathodic deposition of $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ for asymmetric supercapacitors: importance of the electrochemical reversibility of redox couples. *J. Power Sources* **221**, 128–133 (2013).
37. Lu, B. *et al.* Oxygen evolution reaction on Ni-substituted Co_3O_4 nanowire array electrodes. *Int J Hydrogen Energy* **36**, 72–78 (2011).
38. Cao, L., Lu, M. & Li, H.-L. Preparation of mesoporous nanocrystalline Co_3O_4 and its applicability of porosity to the formation of electrochemical capacitance. *J. Electrochem. Soc.* **152**, A871–A875 (2005).
39. Jiang, J. *et al.* Recent Advances in Metal Oxide-based Electrode Architecture Design for Electrochemical Energy Storage. *Adv. Mater.* **24**, 5166–5180 (2012).
40. Hu, C.-C., Hsu, C.-T., Chang, K.-H. & Hsu, H.-Y. Microwave-assisted hydrothermal annealing of binary Ni-Co oxy-hydroxides for asymmetric supercapacitors. *J. Power Sources* **238**, 180–189 (2013).

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Author contributions

J.L. and Q.Y. conceived and designed the experiments. Q.Y. and Z.L. performed the experiments. Q.Y., X.S. and J.L. discussed the results and co-wrote the paper.

Additional information

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