Bowl-shaped NiCo_2O_4 nanosheet clusters as electrode materials for high-performance asymmetric supercapacitors

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ABSTRACT The development of transition metal oxide-based electrode materials with proper controlled structures is highly desirable for high-performance supercapacitors. However, it remains a major challenge. Here, we present the first synthesis of bowl-like NiCo_2O_4 nanosheet clusters through a simple soft template guided hydrothermal strategy. The resulting bowl-like clusters consist of numerous NiCo_2O_4 nanosheets with an average thickness of 19 nm and possess a mean diameter of 1 μm along with a specific surface area of 40 $\text{m}^2 \text{g}^{-1}$. Remarkably, serving as an electrode material in a three-electrode system, the bowl-like NiCo_2O_4 nanosheet clusters exhibit a high specific capacity of 1068 F g^{-1} at a current density of 1 A g^{-1} and excellent cycling stability with 90% capacitance retention after 5000 charge-discharge cycles. Meanwhile, an asymmetric supercapacitor (ASC) assembled with the NiCo_2O_4 clusters and activated carbon (AC) as the two electrodes exhibits a high specific capacitance of 129 F g^{-1} at 1 A g^{-1} , along with a high energy density of 33 W h kg^{-1} at a power density of 0.66 kW kg^{-1} . Such performance is superior to those of many commercial supercapacitors. This study opens a new avenue for the construction of ordered complex particles with controlled architectures for energy storage and conversion applications.

Keywords: bowl-like structure, NiCo_2O_4 nanosheet, cluster, soft template, asymmetric supercapacitors

INTRODUCTION

With the gradual depletion of petroleum resources and increasing global warming, the development of green, sustainable and efficient energy storage devices is of great importance [1–3]. Among various energy storage devices, supercapacitors have been considered as an ideal candidate for green energy storage in terms of their high-power

density, fast charge-discharge speed, and long cycle life [4–6]. Generally, supercapacitors are divided into two categories based on the storage mechanism of electrostatic storage of charges and fast redox reactions on the surface of electrodes, namely, electrical double-layer capacitors and Faradaic pseudocapacitors [4,7]. Compared with the electrical double-layer capacitors, Faradaic pseudocapacitors present high energy density and specific capacitance due to their abundant oxidation states for efficient redox reactions [4,8]. In these devices, transition metal oxides have proven to be ideal electrode materials because of their multiple oxidation states and high theoretical specific capacitance [9]. Moreover, the structure of electrode materials plays a crucial role in determining the electrochemical performance of supercapacitors [10–16]. As a consequence, the development of transition metal oxide electrodes with proper controlled structures is highly desirable for supercapacitors with satisfied performance.

Recently, NiCo_2O_4 has been regarded as a promising candidate for supercapacitor electrodes due to its low cost, easy synthesis, high theoretical capacitance, and environmental friendliness [17–20]. NiCo_2O_4 materials of various structures have been reported as electrode materials, including nanowalls [21], nanorods [22,23], nanowires [24], nanosheets [18,25,26] and nanoflowers [27–29]. However, these NiCo_2O_4 materials show apparent capacitance loss and poor cycling stability owing to the inadequate utilization of their active sites and easy structural collapse during the charge-discharge cycles [21,22,27]. To solve these problems, hollow structures have been developed [20,30–33], which possess large contact areas between the electrode materials and the electrolyte, resulting in more efficient utilization of the

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active materials. Moreover, the presence of void space can alleviate the mechanical strain generated during the fast charge-discharge process, thus improving the cycling stability [31]. However, with excessive void interior space, hollow structures usually show decreased bulk volumetric density when serving as electrode materials, which is disadvantageous to small-volume energy storage devices [5,34,35]. As a unique class of hollow structures, bowl-like structures show an advantage in increasing the volumetric packing density of electrode materials compared with their spherical hollow counterparts, which may contribute to the improvement of volumetric energy density of supercapacitors [36–42]. Meanwhile, it has proven that 2D sheet-like structures favor the electronic/ionic transport in electrodes, thus increasing the specific capacitance and the rate capability [10,11,13–15,43]. Therefore, the combination of the advantages of bowl-shaped structure and unique properties of NiCo_2O_4 nanosheets, yielding bowl-like NiCo_2O_4 nanosheet clusters, is expected to produce promising electrode materials for high-performance supercapacitors. Nevertheless, such materials have remained unexplored thus far.

Here, we demonstrate the first preparation of bowl-like NiCo_2O_4 nanosheet clusters by a simple hydrothermal growth of Ni-Co precursors on the surface of bowl-like sulfonated polystyrene (PS) particles, followed by thermal treatment of the resulting Ni-Co precursor/PS hybrid at 550°C in the air. The interesting bowl-shaped clusters consist of numerous small NiCo_2O_4 nanosheets with an average thickness of 19 nm. The nanosheet clusters possess an average diameter of $1\ \mu\text{m}$ and a high specific surface area (SSA) of $40\ \text{m}^2\ \text{g}^{-1}$. When evaluated as a working electrode in a three-electrode system, the bowl-like NiCo_2O_4 clusters exhibit remarkably high specific capacitance ($1068\ \text{F g}^{-1}$ at $1\ \text{A g}^{-1}$), excellent rate performance (86% at $10\ \text{A g}^{-1}$) and long-time cycling stability (90% after 5000 cycles at $1\ \text{A g}^{-1}$). Compared with their spherical counterparts, i.e., NiCo_2O_4 hollow spheres [30–32,44], electrodes made of such bowl-like NiCo_2O_4 nanosheet clusters show much higher specific capacitance and smaller volume [40]. Furthermore, the bowl-like NiCo_2O_4 nanosheet clusters and commercial activated carbon (AC) were employed as the two electrodes of an asymmetric supercapacitor (ASC). The two different electrodes with complementary working potential windows render the ASC with a large cell voltage of 1.4 V, a high specific capacitance of $129\ \text{F g}^{-1}$ at $1\ \text{A g}^{-1}$ and long-time cycling stability (88% after 5000 cycles at $1\ \text{A g}^{-1}$). Moreover, the supercapacitor delivers a high energy density of $33\ \text{W h kg}^{-1}$ at a power density of

$0.66\ \text{kW kg}^{-1}$. Such excellent performance is superior to those of most reported NiCo_2O_4 -based ASCs [21,22,25,27,45–52] as well as those of many commercial supercapacitors [46,53]. In virtue of the exceptional structure and the outstanding electrochemical performance, the intriguing bowl-like NiCo_2O_4 nanosheet clusters hold promise as electrode materials in energy storage devices.

RESULTS AND DISCUSSION

Structural characterizations

The fabrication procedures of the bowl-like NiCo_2O_4 nanosheet clusters are illustrated in Fig. 1 (experimental details are given in the Supplementary information). Briefly, the emulsion of hollow PS spheres with a uniform diameter of $1\ \mu\text{m}$ (from Dow Company, Figs S1 and S2) was dried under vacuum to convert them into bowl-like hollow particles. Afterwards, the bowl-like PS particles were treated by sulfuric acid to obtain sulfonated PS particles according to the reported procedure [38]. Then, calculated amounts of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ were added into the solution. Driven by the electrostatic interaction between the metal ions and the $-\text{SO}_3\text{H}$ groups, the metal ions could be adsorbed on the surfaces of the bowl-like PS particles [37,38,40]. Through the hydrothermal treatment at 90°C , bowl-like Ni-Co precursor/PS particles were obtained, which were finally converted to the bowl-like NiCo_2O_4 nanosheet clusters *via* thermal annealing at 550°C in the air.

The process of the conversion of the Ni-Co precursor/

Figure 1 Schematic illustration of the fabrication of bowl-like NiCo_2O_4 nanosheet clusters.

PS particles to the NiCo_2O_4 sheet clusters were first examined by thermogravimetric analysis (TGA) in air (Fig. S3a). In the temperature range of 250–420°C, a rapid weight loss is observed; while in the TGA curve of the sulfonated PS template, similar weight loss also occurs (Fig. S3b), suggesting that the weight loss in this temperature range is mainly attributed to the decomposition of the sulfonated PS particles [54,55]. Then in the temperature range of 420–600°C, the curve has reached a plateau with slight weight loss, which can be ascribed to the formation and crystallization of NiCo_2O_4 [54]. Above 600°C, NiCo_2O_4 gradually decomposes to Ni and Co oxides [54]. Accordingly, we treated the Ni-Co precursor/PS particles at 550°C under ambient atmosphere to obtain the NiCo_2O_4 clusters.

The morphologies of the bowl-like PS particles, the Ni-Co precursor/PS hybrid particles and the bowl-like NiCo_2O_4 nanosheet clusters were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a, b show the SEM and TEM images of the bowl-like PS particles, respectively, in which the average wall thickness of the particles is determined to be 150 nm. SEM and TEM images also reveal the beautiful bowl-like structure for the Ni-Co precursor/PS particles, which consist of numerous small nanosheets (Fig. 2c, d). The average shell thickness of the particles is about 450 nm, much larger than the average wall thickness of the PS bowls, indicating that the formed Ni-Co precursors are coated on the surfaces of the PS particles.

The average thickness of the nanosheet layer is measured to be ~140 nm (Fig. 2d). Fig. 2e, f present the SEM and TEM images of the NiCo_2O_4 nanosheet clusters, which well retain the bowl-like structure of their Ni-Co precursor/PS particles. The mean thickness of the NiCo_2O_4 nanosheets is measured to be 19 nm, indicating their ultrathin feature. High-resolution TEM (HRTEM) images clearly show that the distance of two neighboring lattice fringes in the NiCo_2O_4 nanosheets is 0.29 nm (Fig. 2g), which corresponds to the interval spacing of the (220) planes of NiCo_2O_4 crystal [25]. Moreover, the selected area electron diffraction (SAED) pattern presents well-defined diffraction rings, suggesting a polycrystalline characteristic of the NiCo_2O_4 nanosheets (Fig. 2h). Furthermore, elemental mapping images reveal the uniform distribution of Co, Ni and O elements in the NiCo_2O_4 nanosheet cluster (Fig. 2i–l).

Powder X-ray diffraction (XRD) analysis was used to identify the crystal structures of the Ni-Co precursor/PS particles and the NiCo_2O_4 nanosheet clusters (Fig. 3a). It is clear that the diffraction peaks of the Ni-Co precursor/PS particles appear at 11.6°, 33.4°, 38.5°, and 61.1°, which are assigned to the (003), (009), (015), and (110) planes of a Ni-Co hydroxide crystal (JCPDS No. 38-715). The diffraction peaks of the NiCo_2O_4 nanosheet clusters are observed at 18.9°, 31.1°, 36.6°, 44.6°, 59.1°, and 64.9°, corresponding to the (111), (220), (311), (400), (511), and (440) planes of a spinel NiCo_2O_4 crystal (JCPDS No. 20-0781). No additional diffraction peaks are observed, in-

Figure 2 Morphological characterizations. (a) SEM and (b) TEM images of the bowl-like PS particles; (c) SEM and (d) TEM images of the Ni-Co precursor/PS hybrid particles; (e) SEM and (f) TEM images of the bowl-like NiCo_2O_4 nanosheet clusters; (g) HRTEM image and (h) SAED pattern of the bowl-like NiCo_2O_4 nanosheet clusters; (i–l) the corresponding elemental mapping images of (j) Ni, (k) Co, and (l) O.

Figure 3 (a) XRD patterns of the bowl-like Ni-Co precursor/PS hybrid and the bowl-like NiCo₂O₄ nanosheet clusters. (b–d) High-resolution XPS spectra of the bowl-like NiCo₂O₄ nanosheet clusters scratched off from the Ni foam: (b) Co 2p, (c) Ni 2p, (d) O 1s.

dicative of a high purity of the NiCo₂O₄ nanosheet clusters.

To analyze the chemical nature and valence states of the bowl-like NiCo₂O₄ sheet clusters, X-ray photoelectron spectroscopy (XPS) analyses were conducted (Fig. 3 and Fig. S4). It is clear from the survey spectrum that the as-synthesized bowl-like NiCo₂O₄ nanosheet clusters mainly consist of Ni, Co, O, and C elements, and their atomic ratio is close to 1:2:4:3 (Fig. S4), in which the C elements (atom content: 27.3 at%) originate from the carbonization of the PS particle templates. The Co 2p spectrum shows two spin-orbit doublets and two satellites (Fig. 3b). The fitted peaks at 779.5 and 794.5 eV are assigned to Co³⁺, while the other two peaks at 781.0 and 795.9 eV can be attributed to Co²⁺ [18]. The weak satellite peaks at 785.4 and 803.8 eV indicate that most of the cobalt species in the oxide lattice exist in the form of Co³⁺. The Ni 2p spectrum also exhibits two spin-orbit doublets and two satellites (Fig. 3c). The binding energies at 854.0 and 871.1 eV originate from Ni²⁺, while those at 855.9 and 873.8 eV belong to Ni³⁺ [24]. The two high intensity satellite bands at 862.0 and 880.3 eV indicate that the octahedral Ni²⁺ is the major state in the resulting NiCo₂O₄. Thereby, the XPS data demonstrate that the bowl-like NiCo₂O₄ clusters are mainly composed of Co³⁺ and Ni²⁺ ions, which is consistent with the XRD result. On the other hand, the O 1s spectrum shows three deconvoluted bands denoted as O1, O2, and O3, respectively (Fig. 3d). The O1 signal at 529.2 eV corresponds to the metal-oxygen bond while the O2 band at 530 eV is usually as-

sociated with the defects with low oxygen coordination in the material [18]. Meanwhile, the well-resolved O3 peak is probably ascribed to the adsorbed water on the material surface.

The porous characteristic of the bowl-like NiCo₂O₄ nanosheet clusters was analyzed by N₂ adsorption-desorption measurements (Fig. S5). The isotherm profile shows a type IV curve with a small hysteresis loop at a relative pressure of 0.6–1.0, suggesting a mesoporous structure [40], which probably originates from the cluster-like stacking of the NiCo₂O₄ nanosheets. These bowl-like nanosheet clusters possess a Brunauer-Emmett-Teller (BET) surface area of 40 m² g^{−1} and a high Langmuir surface area of 183 m² g^{−1}. Meanwhile, this hierarchical structure shows a mesopore size distribution of 5–30 nm.

Electrochemical measurements

The electrochemical performance of the bowl-like NiCo₂O₄ nanosheet clusters as an electrode material of supercapacitors was first evaluated in a 3.0 mol L^{−1} KOH electrolyte using a three-electrode system, in which the Ni foam coated with the NiCo₂O₄ clusters served as the working electrode, while platinum served as the counter electrode and the saturated calomel electrode acted as the reference electrode. Fig. 4a shows the cyclic voltammetry (CV) curves recorded at different scan rates in a potential window of 0–0.45 V. The shape of CV curves clearly presents a typical pseudocapacitive characteristic [9]. Meanwhile, there are a pair of well-defined redox peaks at 0.20 and 0.40 V, which are ascribed to the Faradaic redox reactions of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺, respectively. The charge storage mechanism is given below [56]:

where M represents Ni or Co ions. Besides, as the scan rate increases from 10 to 100 mV s^{−1}, the anodic and cathodic peaks shift towards the positive and negative potentials, respectively, indicative of a quasi-reversibility of the redox couples [22].

To determine the specific capacitance (C_s), the charge-discharge curves were recorded in a stable voltage window of 0–0.4 V at various current densities (Fig. 4b). Distinct plateaus are observed in the curves, which correspond to the Faradaic charge-discharge process. Moreover, according to the formula:

$$C_s = I\Delta t / \Delta Vm, \quad (3)$$

where I expresses the applied current, Δt denotes the discharge time, ΔV is the voltage change during the discharge, m represents the total mass of the active material in electrode [39], the C_s of the bowl-like NiCo_2O_4 nanosheet clusters reaches 1068, 1036, 986 and 925 F g^{-1} at the current densities of 1, 2, 5 and 10 A g^{-1} , respectively. About 86% of the capacitance is retained as the current density increases from 1 to 10 A g^{-1} , demonstrating the excellent rate performance of the NiCo_2O_4 clusters. Notably, the high C_s of the bowl-like NiCo_2O_4 nanosheet clusters (1068 F g^{-1} at 1 A g^{-1}) is superior to those of many reported NiCo_2O_4 -based electrode materials (Table S1), such as NiCo_2O_4 ball-in-ball hollow spheres (1036 F g^{-1} at 1 A g^{-1}) [44], urchin-like NiCo_2O_4 hollow microspheres (880 F g^{-1} at 1 A g^{-1}) [31] and $\text{C@NiCo}_2\text{O}_4$ hollow spheres (404 F g^{-1} at 1 A g^{-1}) [32].

Electrochemical impedance spectroscopy (EIS) measurements were conducted to verify the charge transfer kinetics of our material. As shown in Fig. 4c, the typical Nyquist curve consists of one depressed semicircle and one rising curve, which correspond to the high frequency region and low frequency region, respectively. The equivalent circuit simulated on the basis of the Nyquist plot is presented in the inset of Fig. 4c [50]. At high frequency, the diameter of the semicircle reflects a low

charge transfer resistance (R_{ct}) of 14 Ω at the electrode-electrolyte interface. While at low frequency, it is clear that the imaginary part sharply increases and the curve has a trend to a vertical line characteristic of capacitive behavior, which responds to the diffusive resistance (Z_w) [50]. Furthermore, the intercept at the real axis stands for the inherent resistance of the whole electrochemical system ($R_s=0.66 \Omega$), related to the sum of the intrinsic resistance of the active materials, the ionic resistance of the electrolyte and the contact resistance between the electrodes and current collector [9]. The negligible R_s indicates excellent conductivity of the bowl-like NiCo_2O_4 sheet clusters. This can be ascribed to the adequate contact between the neighboring bowl-shaped particles and the presence of conductive carbon composition in the clusters, which are favorable for the electron transport [38].

The cycling stability of the bowl-like NiCo_2O_4 nanosheet clusters was also investigated. At the current density of 1 A g^{-1} , around 90% of the initial specific capacitance is retained after 5000 charge-discharge cycles (Fig. 4d). Even at higher current densities (2 and 10 A g^{-1}), about 87% and 83% of the initial specific capacitance are retained, demonstrating the excellent cycling stability. Moreover, SEM images reveal the retention

Figure 4 Electrochemical characterizations of the bowl-like NiCo_2O_4 nanosheet clusters on Ni foam as an electrode material in a three-electrode system. (a) CV curves recorded at varied scan rates from 10 to 100 mV s^{-1} ; (b) charge-discharge voltage profiles at various current densities from 1 to 10 A g^{-1} ; (c) EIS spectrum; (d) cycling performance.

of the bowl-like nanosheet cluster structure of NiCo_2O_4 after 5000 charge-discharge cycles (Fig. S6), indicative of the excellent structural stability of the NiCo_2O_4 clusters.

ASCs can increase the energy density of supercapacitors due to their advanced structures, which consist of a battery-type Faradaic electrode serving as the energy source and a capacitor-type electrode working as the power source [39,57]. Moreover, ASCs can provide a maximum operation window by full use of the different potential windows of the two electrodes, thus increasing their specific capacitance and energy density [8]. With the excellent electrochemical performance evaluated *via* a three-electrode system, the bowl-like NiCo_2O_4 nanosheet clusters were further employed as an anode in a two-electrode ASC, in which porous AC was used as the cathode materials and 3.0 mol L^{-1} KOH was utilized as the electrolyte (denoted as $\text{NiCo}_2\text{O}_4/\text{AC-ASC}$, see electrochemical measurement section in the Supplementary information for details). The ASC maximized the operating voltage of the entire device to 1.4 V. Fig. 5a shows that the CV curve is a quasi-rectangle shape with a small redox peak in the potential window of 0–1.4 V, indicating that the ASC exhibits characteristics of both the double-layer capacitor and the Faraday pseudocapacitor [29]. The

specific capacitance of the $\text{NiCo}_2\text{O}_4/\text{AC-ASC}$ device was calculated from the charge-discharge curves (Fig. 5b) by Equation (3), which reaches 129, 118, 99, and 76 F g^{-1} at 1, 2, 5, and 10 A g^{-1} , respectively. Around 60% of the initial specific capacitance is retained even at a high current density of 10 A g^{-1} , demonstrating good rate performance of $\text{NiCo}_2\text{O}_4/\text{AC-ASC}$. Fig. 5c shows that 88% of the initial specific capacitance is maintained after 5000 charge-discharge cycles at 1 A g^{-1} . When the current density increases to 10 A g^{-1} , 86% of the initial specific capacitance is retained after 5000 cycles, indicative of excellent cycling stability of the ASC device.

The energy density (E) and power density (P) of the $\text{NiCo}_2\text{O}_4/\text{AC-ASC}$ were calculated according to the equations of $E=(1/7.2)C_s V^2$ and $P=3.6E/\Delta t$, respectively, where V is the potential window and Δt represents the discharge time [39]. Remarkably, $\text{NiCo}_2\text{O}_4/\text{AC-ASC}$ exhibits a high energy density of 33 W h kg^{-1} at the power density of 0.66 kW kg^{-1} . Ragone plot reveals that the energy and power densities of our ASC are higher than those of numerous reported NiCo_2O_4 -based ASCs, such as hollow NiCo_2O_4 arrays//N-doped carbon (31.9 W h kg^{-1}) [21], hollow NiCo_2O_4 spheres//AC (21.5 W h kg^{-1}) [48], NiCo_2O_4 nanorods//AC

Figure 5 Electrochemical measurement of the ASC. (a) CV curve at a scan rate of 10 mV s^{-1} ; (b) charge-discharge voltage profiles at various current densities; (c) cycling performance; (d) Ragone plot (inset shows the photograph of a three series-wound ASC powering a red light emitting diode).

(12.6 W h kg⁻¹) [22], hexagonal NiCo₂O₄/AC (24.5 W h kg⁻¹) [50], NiCo₂O₄ nanosheets/Co₃S₄/AC (14 W h kg⁻¹) [26], and others (Fig. 5d and Table S2) [21,27,45,47,49,51,52,58]. Notably, the energy density (33 W h kg⁻¹) of our ASC greatly surpasses those of many commercial supercapacitors (<10 W h kg⁻¹) [46,53]. Furthermore, three NiCo₂O₄/AC-ASCs connected in series may easily illuminate a red-light emitting diode (3 V, 0.015 W) for near 30 s (inset of Fig. 5d), demonstrating the great potential of the bowl-like NiCo₂O₄ nanosheet clusters as electrode materials of high-performance supercapacitors.

The excellent electrochemical performance of the bowl-shaped NiCo₂O₄ sheet clusters can be attributed to their porous architecture along with the bowl-like structure. First, the mesopores formed by the stacking of the NiCo₂O₄ nanosheets not only promote the adequate contact between the active materials and electrolyte, providing abundant reaction sites for the redox reactions, but also facilitate the ion transport, improving the charge storage efficiency. Second, the bowl-like structure of the particles, in comparison with their hollow spherical counterpart, enables an increase in the volumetric packing density and consequently a reduction in the undesirable volume effect of supercapacitor electrodes. Finally, the cavity of the bowl-like clusters may buffer the generated strain in electrolyte during the electrochemical process, thus preventing the collapse of the material, leading to the enhancement of cycling stability.

CONCLUSION

In summary, bowl-like NiCo₂O₄ nanosheet clusters were prepared by a simple soft templating hydrothermal method, using bowl-shaped sulfonated PS particles as the template. The resulting bowl-shaped clusters showed superior electrochemical performance as electrode materials in a three-electrode system, with high specific capacitance (1068 F g⁻¹ at 1 A g⁻¹), superior capacitance retention of 86% at 10 A g⁻¹ and long-time cycling stability (90% after 5000 cycles at 1 A g⁻¹). Furthermore, with porous AC and the NiCo₂O₄ clusters as the two electrodes, an ASC was assembled, which showed a high specific capacitance of 129 F g⁻¹ at 1 A g⁻¹, excellent cycling stability with 88% capacitance retention after 5000 charge-discharge cycles at 1 A g⁻¹, and a high energy density of 33 W h kg⁻¹ at a power density of 0.66 kW kg⁻¹. The excellent electrochemical performance can be attributed to the combination of the bowl-like architecture and the cluster structure of the ultrathin nanosheets. The strategy developed in our study is expected to be applicable to the

construction of diverse ordered complex particles with controlled structures for energy storage and conversion applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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碗型 NiCo_2O_4 纳米片簇应用于高性能不对称超级电容器电极材料

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摘要 开发具有可控结构的过渡金属氧化物基电极材料对于高性能超级电容器尤为重要, 但这仍是其目前面临的重要挑战之一. 本文通过一种简单的软模板水热策略, 首次合成了碗型 NiCo_2O_4 纳米片团簇. 这种碗型团簇由19 nm厚的超薄 NiCo_2O_4 纳米片层构成, 单个团簇平均直径为1 μm , 材料比表面积达到40 $\text{m}^2 \text{g}^{-1}$. 在三电极测试中, 作为电极材料的碗型 NiCo_2O_4 纳米片团簇在1 A g^{-1} 的电流密度下表现出高比电容值(1068 F g^{-1}), 且循环5000次后仍有90%的电容保有率. 此外, 以该 NiCo_2O_4 团簇和活性炭作为电极材料组装而成的不对称超级电容器在1 A g^{-1} 的电流密度下展示出129 F g^{-1} 的比电容; 在0.66 kW kg^{-1} 功率密度下, 能量密度高达33 W h kg^{-1} . 这些性能优于大部分商业化的超级电容器. 本研究为构筑面向能量储存和转换应用的结构可控的新型有序过渡金属氧化物材料开辟了新途径.