Ni(OH)₂ nanoflakes supported on 3D hierarchically nanoporous gold/Ni foam as superior electrodes for supercapacitors

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ABSTRACT The increasing demand for portable electronic devices and hybrid electric vehicles stimulates the development of supercapacitors as an advanced energy storage system. Here, we demonstrate a binder-free nickel hydroxide@nanoporous gold/Ni foam (Ni(OH)₂@NPG/Ni foam) electrode for high-performance supercapacitors, which is prepared by a facile three-step fabrication route including electrodeposition of Au-Sn alloy on Ni foam, chemical dealloying of Sn and electrodeposition of Ni(OH)₂ on NPG/Ni foam. Such Ni(OH)₂@NPG/Ni foam electrode is composed of a thin layer of conformable Ni(OH)₂ nanoflakes supported on three-dimensional (3D) hierarchically porous NPG/Ni foam substrate. The resulting Ni(OH)₂@NPG/Ni foam electrode can offer highways for both electron transfer and ion transport and lead to an excellent electrochemical performance with an ultrahigh specific capacitance of 3,380 F g⁻¹ at a current density of 2 A g⁻¹. Even when the current density was increased to 50 A g⁻¹, it still retained a high capacitance of 1,927 F g⁻¹. The promising performance of the Ni(OH)₂@NPG/Ni foam electrode is mainly ascribed to the 3D hierarchical porosity and the highly conductive network on the NPG/Ni foam composite current collector, as well as the conformal electrodeposition of Ni(OH)₂ active material on the NPG/Ni foam, which induces the formation of interconnected porosity both on the top surface and on the inner surface of the electrode. This inspiring electrochemical performance would make the as-designed electrode material become one of the most promising candidates for future electrochemical energy storage systems.

Keywords: supercapacitor, nanoporous gold, nickel hydroxide, electrode material, hierarchical porosity.

INTRODUCTION

With the increasing global demand for renewable and sustainable high-power energy resources for the use in portable electronic devices, electric vehicles (EVs) and hybrid electric vehicles (HEVs), high performance electrochemical energy storage systems such as Li-ion batteries (LIBs) and supercapacitors have attracted considerable attention recently [1]. Compared with LIBs, supercapacitors possess faster charge/discharge rates, higher power density and longer cycle life but lower energy density [2]. Supercapacitors can be divided generally into electrical double layer capacitors (EDLCs) and pseudocapacitors according to their energy storage mechanism [3]. EDLCs store energy based on reversible ion adsorption at the electrode/electrolyte interface, while pseudocapacitors also utilize fast and reversible Faradaic redox reactions at the electrode surface, thus giving a larger capacitance and higher energy density than EDLCs [4]. It is well known that the nature of the electrode materials plays a very important role in the electrochemical performance of pseudocapacitors. Among various pseudocapacitor electrode materials, transition-metal oxides/hydroxides (TMOs/TMOHs), including RuO₂ [5,6], MnO₂ [7,8], Co(OH)₂ [9,10] and Ni(OH)₂ [11,12], have been the most commonly employed electrode materials for decades. Compared to other TMOs/TMOHs, Ni(OH)₂ has been regarded as the most promising electrode material due to its low cost, ultrahigh specific capacitance [13] and environmental friendliness. Moreover, the layered structure of Ni(OH)₂ could provide a large number of active sites for ions storage, which makes it an

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attractive candidate electrode material for high performance supercapacitors. However, the high electrochemical performance is usually very challenging to be achieved in practice owing to the intrinsically poor electrical conductivity of $\text{Ni}(\text{OH})_2$ (in the order of $10^{-17} \text{ S cm}^{-1}$ at room temperature) [14]. In order to address the poor conductivity issue, a number of highly conductive 3D multifunctional substrates, such as Ni foam [15,16], carbon nanotubes [17,18], graphene [19,20] and combinations of these materials [21–23], have been used as the frameworks to grow the active $\text{Ni}(\text{OH})_2$ electrode material to boost its pseudocapacitive performance. These substrates could provide both fast transport channels for ions diffusion and interconnected wall structures for electron transfer in electrodes. It is thus anticipated that supercapacitor electrode materials with 3D porous structures would exhibit an enhanced electrochemical performance.

In recent years, highly nanoporous gold (NPG) [24] with excellent electrical conductivity and high chemical stability has also been employed as the supporting substrate for pseudocapacitive electrodes to improve their electrochemical performance [25–27]. As mentioned above, the continuous porous structure of NPG can offer rapid pathways for electron and ion transport, significantly enhancing the rate capability of the pseudocapacitive electrode materials. However, the NPG films used in these studies are usually prepared by chemical dealloying of a commercial available gold leaf (e.g., Au–Ag alloy foil), producing a very thin free-standing NPG film which is brittle and difficult to be integrated with other substrates. Moreover, up to now, the electrode structure design is still mainly based on low surface area, 2D planar substrates, which limits the loading amount of electrode materials and restricts the penetration of electrolyte [28]. So far, there has been no report on the integration of NPG-based electrode materials in a 3D framework structure to improve the capacitive performance. In this context, it is necessary to develop a facile and reliable method for fabricating 3D NPG-integrated substrates.

Recently, we have demonstrated that NPG films can be well grown on various conductive substrates, such as copper foil, stainless steel and Ni foam, through a facile procedure that combines electrodeposition and chemical dealloying of the Au–Sn alloy film [29–33]. The seamless integration of NPG films with these frequently-used conductive substrates is of great value to widen the application range of NPG-based materials. In this work, we develop a nanostructured electrode by electrodeposition

of $\text{Ni}(\text{OH})_2$ nanoflakes on NPG/Ni foam composite substrate ($\text{Ni}(\text{OH})_2$ @NPG/Ni foam) as a high-performance electrode material for pseudocapacitors. When functioning as a supercapacitor electrode, such appropriately designed $\text{Ni}(\text{OH})_2$ @NPG/Ni foam possesses many advantages: (i) highly conductive NPG film grown on Ni foam substrate acts both as the framework and the highway for electron transfer; (ii) the thin $\text{Ni}(\text{OH})_2$ film conformably wrapped round the NPG ligament surfaces provides a large electrode/electrolyte interface and a short pathway for ions diffusion, thus facilitating a fast Faradaic reaction; (iii) both $\text{Ni}(\text{OH})_2$ and NPG are homogeneously distributed and firmly supported on the Ni foam substrate, eliminating the use of any conductive agent or polymeric binder, which simultaneously reduces the impedance and significantly increases the effective surface area of the electrode material. Benefiting from these characteristics, the 3D hierarchical porous $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode material exhibits an enhanced supercapacitive performance with ultrahigh specific capacitance, good rate capability and relatively excellent cycling stability.

EXPERIMENTAL SECTION

Preparation of electrodes

All used chemicals were of analytical grade and purchased from Aladdin (Shanghai, China). Ni foam (0.5 mm thick, Changsha Lyrun Material Co. Ltd., China) was employed as not only the substrate for the electrodeposition of Au–Sn alloy film, but also the current collector for the supercapacitor electrode. The fabrication procedure for the $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode is illustrated in Fig. 1. Firstly, Ni foam substrates were sequentially treated with acetone, alcohol, deionized water and 4% hydrochloric acid for 30 min in an ultrasonic bath before use. Then, Au–Sn alloy films were electrodeposited on the as-pre-treated Ni foam substrate as reported in our previous studies [29–33]. Briefly, the electrodeposition process was carried out using a DC power supply in a one-compartment two-electrode cell with a Pt mesh as the counter electrode and Ni foam substrates (1 cm^2 exposure area) as the working electrodes. The Au–Sn alloy films were galvanostatically electrodeposited on Ni foam substrates under a current density of 5 mA cm^{-2} at 45°C for 20 min. The Au–Sn alloy film modified Ni foam substrates (AuSn/Ni foam) were then immersed in a 5 mol L^{-1} NaOH and 1 mol L^{-1} H_2O_2 solution for one week at room temperature to completely dealloy the Sn component, thus resulting in the transformation from Au–Sn alloy to the NPG on the

Figure 1 Schematic illustration of the fabrication procedure for the Ni(OH)₂@NPG/Ni foam electrodes.

Ni foam substrates (NPG/Ni foam). Finally, the electrodeposition of Ni(OH)₂ was conducted using a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) in a one-compartment three-electrode cell with the as-prepared NPG/Ni foam, a platinum plate and a saturated calomel electrode (SCE) served as the working electrode, the counter electrode and the reference electrode, respectively. The electrodeposition process was performed in galvanostatic mode at a current density of 0.2 mA cm⁻² for 35 min at room temperature in a aqueous electrolyte containing 0.01 Ni(NO₃)₂ and 0.01 mol L⁻¹ NaNO₃. After electrodeposition, the as-prepared Ni(OH)₂@NPG/Ni foam electrodes were thoroughly rinsed with deionized water and dried in air. For comparison, Ni(OH)₂ was also directly deposited on the bare Ni foam substrates under the same conditions to yield the Ni(OH)₂@Ni foam electrodes. The mass of the electrodeposited Ni(OH)₂ was about 0.25 mg estimated by Faraday's law.

Characterization

The surface morphology of the samples was characterized using a field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL). The crystal structures of the electrodes were analyzed by X-ray diffraction (XRD, Rigaku D/max-2200/PC) using a Cu K α radiation source at a wavelength of 0.1541 nm. The chemical composition of Ni(OH)₂ was determined by high-resolution X-ray photoelectron spectroscopy (XPS, ESCALab250) with Al K α radiation. The electrochemical performance of the Ni(OH)₂@NPG/Ni foam electrodes was evaluated in a standard three-electrode set-up with the Ni(OH)₂@NPG/Ni foam electrodes, a platinum plate and a SCE electrode used as the working electrodes, the counter electrode and

the reference electrode, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were performed using a CHI660E electrochemical workstation in a 1 mol L⁻¹ KOH aqueous electrolyte at room temperature. Specifically, CV tests were conducted between 0 and 0.5 V (vs. SCE) at different scan rates of 1, 5, 10, 15, 20, 30, 40 and 50 mV s⁻¹. GCD curves were collected at different current densities of 2, 5, 8, 10, 15, 20, 30, 40 and 50 A g⁻¹. EIS measurements were performed by applying an AC voltage with 5 mV amplitude within the frequency range from 100 kHz to 0.01 Hz under open circuit potential conditions.

RESULTS AND DISCUSSION

The morphological characterization of the pristine Ni foam, the NPG/Ni foam and the integrated Ni(OH)₂@NPG/Ni foam electrode are shown in Fig. 2. Fig. 2a shows a digital photograph of these samples, respectively. It was observed that there was a uniform growth of NPG film on the Ni foam surface which has completely turned from silvery into brown color. It is noted that the as-prepared NPG film was still well-adhered to the Ni foam surface even after thoroughly rinsing with deionized water, revealing that the NPG/Ni foam has undergone a reliable binder-free integration, allowing it to be employed as an excellent composite current collector. After electrodeposition of Ni(OH)₂, the NPG/Ni foam composite became a little darker, indicating the formation of Ni(OH)₂ on the NPG/Ni foam surface. Owing to the flexibility of the Ni foam substrate, the Ni(OH)₂@NPG/Ni foam electrode exhibited good flexibility as shown in the inset of Fig. 2a. The structure and surface morphology of the pristine Ni foam substrate displays its 3D interconnected porous feature (Fig. 2b) with a relatively smooth surface (Fig. 2c). After sequential electrodeposition and chemical dealloying of the Au-Sn alloy film, a NPG film was uniformly present on the skeleton of the Ni foam, as shown in the lower magnification SEM images (Fig. 2d, e). A higher magnification SEM image shows that the NPG film was made up of vertically aligned and well interconnected gold nanowalls with hierarchical porosity (Fig. 2f). The mechanism behind the vertically oriented growth of the porous gold nanowalls is not completely understood at this time. As can be observed from Fig. 2g, the uniform and porous nanoarchitecture is composed of quasi-periodic interconnected nanoporous channels and gold ligaments with a characteristic size of ~100 nm. The cross-sectional SEM image of the NPG film reveals that such bicontinuous structure was very uniform across the

Figure 2 Photograph of a 1×1 cm² Ni foam, 1×1 cm² NPG/Ni foam composite and 1×1 cm² Ni(OH)₂@NPG/Ni foam electrode. Inset: a Ni(OH)₂@NPG/Ni foam electrode bent to illustrate its good flexibility (a); Top-view SEM images of the pristine Ni foam (b, c) and the NPG/Ni foam composite (d–g) under different magnifications, and the cross-sectional SEM image of the NPG film (h).

entire film thickness, which is approximately 1.4 μm thick (Fig. 2h). The detailed fabrication procedure and the typical corresponding microscope images of the samples during the NPG/Ni foam preparation process can be found in our previous reports [28–32]. According to the mercury porosimetry analysis (Fig. S1), the specific surface area of the bare Ni foam and the NPG/Ni foam is 0.055 and 0.147 m² g^{−1}, respectively. As a current collector, the NPG/Ni foam composite not only offers highly conductive pathways, but also shortens the distance of the ion diffusion, which is beneficial for the high performance of electrode materials.

Further, Ni(OH)₂ was galvanostatically electrodeposited as the active material on the as-prepared NPG/Ni foam composite. The low-magnification SEM images show that the Ni(OH)₂ films were uniformly deposited on the ligaments of the NPG/Ni foam composite (Fig. 3a, b),

Figure 3 Top-view SEM images of Ni(OH)₂@NPG/Ni foam electrode under different magnifications (a–c), and the corresponding cross-sectional SEM image (d).

while the higher magnification SEM image from the top view reveals that the Ni(OH)₂ nanoflakes were densely wrapped on the NPG ligaments (Fig. 3c). It can also be observed that the deposition of Ni(OH)₂ nanoflakes not only maintains the interconnected sub-micron porous features originating from the NPG structures, but also forms its own interconnected morphology with nanoporosity. Such a hierarchical interconnecting porous network may provide a path for charge and mass transfer in electrochemical kinetics. Additionally, cross-sectional SEM image (Fig. 3d) displayed that a very thin Ni(OH)₂ layer was also electrodeposited on the inner nanopore channels of the NPG structure, suggesting the original nanoporous structure of the NPG film was well preserved. Further characterization of the electrode was conducted by the TEM analysis (Fig. S2). Therefore, the Ni(OH)₂ active materials were electrodeposited not only on the top surface, but also the inner surfaces of the NPG film. It has been concluded that the active material in each position plays a different role [28], namely, the top surface Ni(OH)₂ determines the overall capacitance, while the inner surface Ni(OH)₂ influences the capacitance performance. The Ni(OH)₂@NPG/Ni foam electrodes prepared by the three-step fabrication procedure exhibit an integrated structure in which the Ni foam provides a 3D interconnected framework and the bicontinuous NPG film serves as a high surface area and highly conductive support to yield a uniform electrodeposition of Ni(OH)₂ nanoflakes. Such an integrated electrode architecture may substantially improve the intimate contact between the Ni(OH)₂ nanostructures and the NPG/Ni foam composite current collector to produce a binder- and additive-free

Figure 4 XRD patterns of the NPG/Ni foam composite and the Ni(OH)_2 @NPG/Ni foam electrode (a), and XPS spectrum of Ni 2p orbitals for the Ni(OH)_2 electrodeposited on the NPG/Ni foam composite (b).

electrode. Moreover, the preserved interconnected porosity both on the top surface and in the inner parts of the NPG structure after Ni(OH)_2 electrodeposition may induce a remarkably beneficial effect on the kinetic properties during electrochemical processes. For comparison, the Ni(OH)_2 film was also directly electrodeposited on the pristine Ni foam substrate (Ni(OH)_2 @Ni foam). It can be seen from Fig. S3 that the obtained material has a porous structure with densely deposited Ni(OH)_2 nanoflakes on the Ni foam surfaces.

The crystal structures of the NPG/Ni foam composite and the Ni(OH)_2 @NPG/Ni foam electrode were characterized by XRD (Fig. 4a), whereby the diffraction peaks at $2\theta = 44.5^\circ$, 51.8° and 76.4° can be sequentially indexed to the (111), (200) and (220) planes of the face centered cubic (fcc) phase of Ni (JCPDS File No. 04-0850), while the diffraction peaks at $2\theta = 38.2^\circ$, 44.5° , 64.7° and 77.7° can be well indexed to the (111), (200), (220) and (311) planes of fcc Au (JCPDS File No. 04-0784), respectively. It should be noted that the cubic Ni(111) peak almost overlaps the cubic Au (200) peak. There are no evident peaks related to Ni(OH)_2 in the pattern, indicating that the electrodeposited Ni(OH)_2 film has intrinsically poor crystallinity, which was further confirmed by the selected area electron diffraction (SAED) investigation (Fig. S2a, Inset) and the HR-TEM image (Fig. S2b). Furthermore, the chemical state of the Ni element was characterized by high-resolution XPS, as shown in Fig. 4b. There are two typical peaks at the binding energies of 855.4 and 873.1 eV with a separation of 17.7 eV in the XPS spectrum, which can be attributed to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ orbitals of Ni(OH)_2 , respectively[34].

In order to evaluate the electrochemical performance of the as-prepared 3D hierarchical porous electrodes, CV and GCD measurements were conducted on the Ni(OH)_2 @NPG/Ni foam electrode in 1 mol L^{-1} KOH

aqueous solution. For comparison, the Ni(OH)_2 @Ni foam electrode was characterized under the same conditions (Fig. S4). Fig. 5a shows the typical CV curves of the Ni(OH)_2 @NPG/Ni foam electrode with a Ni(OH)_2 loading amount of $\sim 0.25 \text{ mg cm}^{-2}$ within a potential window from 0 to 0.5 V at different scan rates. A pair of well-defined redox peaks, which was related to the reversible redox reaction of $\text{Ni}^{2+}/\text{Ni}^{3+}$, can be clearly identified in the CV curves, indicating that the capacitance characteristics mainly results from Faradaic redox reaction. As well known for the Ni(OH)_2 electrode materials, the surface reaction can be illustrated as $\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + \text{e}^-$, which involves the intercalation and deintercalation of protons [35–37]. Such results suggest that the charge storage mechanism of the Ni(OH)_2 @NPG/Ni foam electrode should be mainly attributed to the Ni(OH)_2 nanoflakes. The anodic and cathodic peaks observed in the CV curves are symmetric, indicating the excellent reversibility of the as-prepared Ni(OH)_2 @NPG/Ni foam electrode. In addition, the potentials of the redox peaks shift with increasing scan rate, indicating a rate-limiting process for the redox reversibility of the electrode [38, 39], while the large potential separation ($> 0.1 \text{ V}$) between the oxidation and reduction peaks suggests a fine battery behavior [40]. The specific capacitances of the Ni(OH)_2 @NPG/Ni foam electrode and the Ni(OH)_2 @Ni foam electrode, calculated from the CV curves at various scan rates according to the formula, $C_s = \int idv / 2mUs$, where C_s , i , m , U and s represent the specific capacitance, current density, mass of active materials, potential window and scan rate, respectively (Fig. 5b). It is shown that the Ni(OH)_2 @NPG/Ni foam electrode exhibits significantly enhanced capacitive performance compared with that of the Ni(OH)_2 @Ni foam electrode, with the highest specific capacitance value of $3,711 \text{ F g}^{-1}$ achieved at a scan rate of 1 mV s^{-1} . To the best of our knowledge,

Figure 5 Typical CVs of the Ni(OH)₂@NPG/Ni foam electrode (a) and the specific capacitance of the Ni(OH)₂@NPG/Ni foam electrode and the Ni(OH)₂/Ni foam electrode at various scan rates (b). GCD curves of the Ni(OH)₂@NPG/Ni foam electrode (c) and the specific capacitance of the Ni(OH)₂@NPG/Ni foam electrode and the Ni(OH)₂/Ni foam electrode at various current densities (d).

this is the highest value among the reported supercapacitor electrode materials. The best values of Ni(OH)₂ based electrodes reported in the literature are 3,152 F g⁻¹ for Ni(OH)₂/Ni foam electrode [15] and 3,300 F g⁻¹ for Ni(OH)₂@CNT/Ni foam electrode [21]. Moreover, the specific capacitance of the Ni(OH)₂@NPG/Ni foam electrode remains 1,645 F g⁻¹ at a scan rate of 50 mV s⁻¹. The current collector plays a very important role in the electrochemical performance of the electrode material [41–43]. Such ultrahigh specific capacitance and excellent rate capability of the Ni(OH)₂@NPG/Ni foam electrode could be mainly attributed to the significantly enhanced charge transport benefiting from the seamlessly integrated binder- and additive-free electrode with 3D hierarchical micro/nanoporosity, which makes full use of the conformally wrapped Ni(OH)₂ nanoflakes on the high surface area NPG/Ni foam composite current collector. The ultrahigh specific capacitance of the Ni(OH)₂@NPG/Ni foam electrode was further confirmed by GCD measurements under different current densities. A slightly narrower potential window from 0 to 0.45 V was chosen in order to avoid an overestimation of the specific capacitance value due to the oxygen evolution reaction in the high potential range [44]. As shown in Fig. 5c, the GCD

curves of the Ni(OH)₂@NPG/Ni foam electrode exhibits a typical pseudocapacitive behavior, with the voltage plateau corresponding to the redox peaks displayed in the CV curves (Fig. 5a). The specific capacitance of the Ni(OH)₂@NPG/Ni foam electrode and the Ni(OH)₂/Ni foam electrode can also be calculated from the GCD curves, according to the equation, $C_s = i\Delta t/mU$, where C_s , i , Δt , m and U represent the specific capacitance, current density, discharge time, mass of active materials and potential window, respectively. It is shown that the Ni(OH)₂@NPG/Ni foam electrode exhibits greatly improved capacitance performance, with a specific capacitance as high as 3,380 F g⁻¹ at a charge/discharge current density of 2 A g⁻¹ and 57% (1,927 F g⁻¹) capacitance retention at 50 A g⁻¹, demonstrating a relatively good rate capability (Fig. 5d).

For a deep understanding of the supercapacitive performance of the as-prepared electrodes, the Nyquist plot of the Ni(OH)₂@NPG/Ni foam and the Ni(OH)₂/Ni foam electrodes in the frequency range from 0.01 Hz to 100 kHz at open-circuit potential with an AC amplitude of 5 mV are shown in Fig. 6a. The shapes of the Nyquist plots for the two electrodes are composed of a semicircle in the high frequency range and a straight line in the low

Figure 6 Nyquist plots of the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode and the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode (a), with a magnification of the high frequency region in the bottom right inset and an equivalent circuit model in the top right inset (a). Cycling stability of the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode and the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode as a function of the cycle number at a current density of 30 A g^{-1} (b).

frequency region, which are associated with the interfacial charge transfer process and the diffusion process of the electrolyte ions into the interior part of the electrodes, respectively. At very high frequencies, the intercept with the real axis (Z') reflects the equivalent series resistance (ESR) in the electrode/electrolyte system, consisting of the resistance of the electrode and the ionic resistance of the electrolyte. The lower internal resistance of the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode compared with that of the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode is mainly ascribed to the larger interfacial areas between the active Ni(OH)_2 on the 3D hierarchically NPG/Ni foam composite current collector and the electrolyte, which provides shortened charge transfer distances. In the high frequency region, it can be seen that the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode displays a much smaller semicircle than that of the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode, which indicates an improved interfacial charge transfer. While in the low frequency region, the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode presents a steeper straight line than that of the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode, which indicates a smaller diffusive resistance and better access of the electrolyte ions into the electrode material. All these results prove that the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode exhibits faster charge transfer and easier ion diffusion, which are responsible for its enhanced capacitive performance. An equivalent circuit model based on the EIS results (Fig. S5) was proposed in the inset in Fig. 6a, where R_s represents the ohmic resistance and can be determined from the intercept of the Nyquist plot to the real axis, R_{ct} is the charge transfer resistance between active materials and electrolyte ions, which can be deduced from the semicircle diameter in the Nyquist plot, Z_w is the Warburg resistance of ionic diffusion from the electrolyte to the electrode surface, and constant phase elements (CPEs) are

used in place of the double-layer capacitor owing to the surface roughness and distribution of the reactions on the electrode surface. With NPG decoration, the R_s decreases from 0.67 to 0.59Ω . The fitting R_{ct} values for $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ and $\text{Ni(OH)}_2\text{@Ni foam}$ electrode are 0.94 and 24.1Ω , respectively. It can be concluded that the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode with much lower R_s and R_{ct} value significantly promotes the electrochemical reaction at the interface between the electrode and the electrolyte. The cycling stability is another important property for a supercapacitor electrode material intended for long-term application. The cycling stability of the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode and the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode was examined by means of GCD cycling between 0 and 0.45 V at a current density of 30 A g^{-1} . The GCD curves of the $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode (Fig. S6) clearly reveal the highly reversible characteristics of the charge/discharge process. Cycling was continuously conducted for a total of $5,000$ cycles, and the specific capacitance retention with cycling is shown in Fig. 6b. It can be observed that the specific capacitance of $\text{Ni(OH)}_2\text{@NPG/Ni foam}$ electrode showed a rapid loss of about 31.2% of its initial value in the first $1,000$ cycles and then remained relatively constant in the subsequent $4,000$ cycles, in comparison with a serious 64% capacitance loss of the $\text{Ni(OH)}_2\text{@Ni foam}$ electrode after $1,000$ cycles under the same conditions. As reported in a previous study, the choice of substrate has a significant effect on the cyclic stability of the electrode material, and Ni foam substrate is regarded as an inferior substrate to exhibit a poor cyclic stability for the TMOH-based electrode material since the formation of nickel oxide on the Ni foam surface leads to increased resistance between the electrode material and the current collector [41]. With NPG decoration on Ni foam, the R_s for $\text{Ni(OH)}_2\text{@NPG/}$

Figure 7 Top-view SEM images of the $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode under different magnifications after charge/discharge cycling (a–c), and the corresponding cross-sectional SEM image (d).

Ni foam and $\text{Ni}(\text{OH})_2$ @Ni foam electrodes decreases from 0.67 to 0.59 Ω , and R_{ct} from 24.1 to 0.94 Ω . Therefore, it can be concluded that the introduction of the NPG nanostructure is beneficial to an improved cycling stability of the $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode. Furthermore, the surface morphology of the $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode after charge/discharge cycling was characterized and the results were shown in Fig. 7. It can be seen from the low magnification SEM images (Fig. 7a, b) that the ligament surfaces still exhibits a smooth and uniform morphology, while the higher magnification SEM images (Fig. 7c, d) reveal that the $\text{Ni}(\text{OH})_2$ nanoflakes have become rougher after cycling. Meanwhile, the interconnected porosity, both on the top surface and in the inner surface of the NPG film, is well maintained, which could guarantee the easy infiltration of the electrolyte, the short ion transport distances and the uninterrupted pathways for charge transfer.

CONCLUSIONS

In summary, we have developed a robust 3D hierarchically porous $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode as a superior electrode material for supercapacitors, with ultrahigh specific capacitance, remarkable rate capability and excellent cycling stability. The superior electrochemical performance of the as-prepared electrode can be attributed to the following aspects of its unique electrode structure. Firstly, the interconnected macropores within the 3D Ni foam substrate can act as an ion-buffering reservoir to shorten the ion diffusion length from the bulk electrolyte to the inner electrode surfaces. In addition, the high porosity in both the NPG film and the

surface-anchored $\text{Ni}(\text{OH})_2$ nanoflakes layer can further improve the ion transport and charge storage capability. Secondly, the conductive NPG-based nanostructured 3D construction together with the Ni-foam-based macrostructured 3D networks can supply multidimensional electron pathways for rapid electronic transport during charge/discharge processes. Finally, the tight connections among the individual components promise a robust integrated electrode without any need for inactive components (e.g., conducting additives and binders), as well as a 3D hierarchically porous structures which leads to highly efficient electron transfer and ion transport. These outstanding characteristics of the 3D hierarchically porous $\text{Ni}(\text{OH})_2$ @NPG/Ni foam electrode will make it a promising candidate for high performance supercapacitors.

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

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三维分级结构氢氧化镍纳米片@纳米多孔金/泡沫镍超级电容器电极材料

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摘要 人们对便携式电子器件和混合动力汽车的需求不断增长, 激发了超级电容器等先进储能体系的发展. 本文通过三步法, 包括电化学沉积金-锡合金、化学去合金除锡以及电化学沉积氢氧化镍等, 制备了无需粘结剂的氢氧化镍@纳米多孔金/泡沫镍电极用作超级电容器电极材料. 该电极材料由支撑在三维分级多孔的纳米多孔金/泡沫镍基底表面的氢氧化镍纳米片薄层组成, 能够为电子传导与离子输运提供快速通道, 在 2 A g^{-1} 的充放电电流密度下比电容值高达 3380 F g^{-1} , 当充放电电流密度增大到 50 A g^{-1} 时, 其比电容值仍能保持为 1927 F g^{-1} , 表现出优异的电化学性能. 氢氧化镍@纳米多孔金/泡沫镍电极材料具有优良电化学性能的原因在于其所拥有的三维分级多孔结构、纳米多孔金/泡沫镍复合集流体的高导电网络以及氢氧化镍活性材料在纳米多孔金/泡沫镍表面的保形电沉积使整个电极的内外表面均形成互连的多孔结构. 氢氧化镍@纳米多孔金/泡沫镍电极材料所展现出的优异电化学性能令其有望成为未来最有前景的电化学储能材料之一.