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Research on the High-Performance Electrochemical Energy Storage of a NiO@ZnO (NZO) Hybrid Based on Growth Time

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Abstract: A NiO@ZnO (NZO) hybrid with different reaction times was successfully synthesized by a green hydrothermal method. After comparison, it was found that hydrothermal time had a great impact on specific capacitance. As a supercapacitor electrode of NZO-12h, it exhibited the maximum reversible specific capacitance of 985.0 F/g (3.94 F/cm^2) at 5 mA/cm² and 587.5 F/g (2.35 F/cm^2) at 50 mA/cm², as well as a high retention of 74.9% capacitance after 1500 cycles at 20 mA/cm². Furthermore, the asymmetric electrode device with ZnO-12h and activated carbon (AC) as the positive and negative electrodes was successfully assembled. In addition, the device exhibited a specific capacitance of 85.7 F/g at 0.4 A/g. Moreover, the highest energy density of 27.13 Wh kg⁻¹ was obtained at a power density of 321.42 W kg⁻¹. These desirable electrochemical properties demonstrate that the NZO hybrid is a promising electrode material for a supercapacitor.

Keywords: NiO@ZnO; electrochemical performance; supercapacitor

1. Introduction

The development of industrialization has caused tremendous pressure on the environment, and it has also seriously affected people's lives. It is necessary to find sustainable and renewable resources [1]. Supercapacitors, excellent energy storage devices, can effectively alleviate the current energy crisis [2–4]. Based on their obvious advantages, such as simple design, high-power density, long cycling lifetime, and short charge/discharge rate [5–7], supercapacitors have attracted much research interest in recent years. However, their development has been limited due to low-energy density, making it difficult to obtain a capacitor with both high-energy density and good power density [8–10]. It is important to find an effective solution to improve the performance of the electrode material.

As an excellent candidate, transition metal oxide can obtain good capacitance characteristics benefiting from its various oxidation states [11]. Nickel oxide (NiO), a low-toxicity and high theoretical specific capacity electrode material, has been widely investigated for energy storage devices [12]. Until now, research on nickel-based materials has made great progress for supercapacitors [13,14]. Gund et al. [14] fabricated micro-belts like β -Ni(OH)₂ thin films, and its specific capacitance was 462 F/g at 5 mV/s. As is known, the structure of a material has a direct influence on its performance. To some extent, structural limitations make the conductivity of transition metal oxide unsatisfactory, so that the actual specific capacitance is lower than the theoretical value [15]. It is reported that the electrochemical property of mixed transition metal oxide is superior to single transition metal



oxides, and the former can display the synthetic effect of each component. Currently, considerable efforts have been devoted to developing the materials, which exhibit improved electrochemical performance [16–18].

As a single-crystal material, zinc oxide (ZnO) possesses excellent properties, such as wide band gap (3.7 eV), a high-energy density of 650 Ah/g, and excellent chemical stability [19–22]. In addition, the electrical conductivity of ZnO can achieve 230 S/cm [23]. Thus, ZnO can be used as a potential electrode material [24–27]. For example, Hou et al. [27] reported that the ZnO/NiO hierarchical core-shell structure exhibits enhanced pseudocapacitive behaviors, owing to synergistic effect of combining ZnO and NiO/MoO₂ composite. Based on this theory, a hybrid (NZO) was prepared by combining NiO and ZnO in our work. The flower-like NZO electrode material has a large surface area, allowing the electrolyte solution to have more contact with the active material. Thus, NZO electrode material has enhancing electrochemical performance.

In this study, NZO on Ni foam with different reaction times was fabricated using a simple and fast hydrothermal method. Their structure and electrochemical properties were also investigated successfully. It was found that NZO-12h exhibits the best electrochemical performance compared with other electrode materials. Further, it shows a high specific capacitance of 3.94 F/cm² at 5 mA/cm² and high rate capability of 59.6% due to its synergistic properties, growth on conductive substrate, and unique flower-like structure.

2. Materials and Methods

All reagents required for the experiment were of analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The NZO was prepared using a facile hydrothermal method. First, Ni foam (2 cm \times 2 cm) was pretreated with 5% HCl solution to remove the oxide layer on its surface, and then it was ultrasonically washed with acetone, ethanol, and deionized (DI) water for the same time, with each step sustained for 15 min. Then, 2 mmol nickel nitrate, 4 mmol zinc nitrate, and 24 mmol urea were dispersed into 50 mL DI water with continuous stirring for 30 min to form a green transparent solution. The solution was transferred into a 100 mL autoclave and a piece of pre-treated Ni foam immersed. The autoclave was sealed and heated at 373 K for 12 h to carry out the hydrothermal reaction, and then naturally cooled to room temperature. Next, the Ni foam was rinsed with DI water and ethanol several times, and dried it at 333 K for 5 h. Finally, cleaned Ni foam was put in the tube furnace at 523 K for 2 h, heating rate 5 °C/min, and the product was labeled as NZO-12h. In order to study the effect of hydrothermal time on the properties of electrode materials, analogous methods were used to fabricate other NZO samples with different reaction times of 3 h, 6 h, and 24 h. These samples were denoted as NZO-12h is shown in Figure 1.

As-prepared products were analyzed using X-ray diffraction (XRD) measurements and recorded with a Rigaku D/max 2500PC diffractometer with Cu Ka radiation ($\lambda = 0.154156$ nm). X-ray photoelectron spectroscopy (XPS) was taken through an ESCA-LAB Mk II (Vacuum Generators) spectrometer (Thermo Electron Corporation, New York, America). The morphology and microstructure of the as-prepared sample were characterized by field emission scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) and transmission electron microscope (TEM, Tecnai F30G2, FEI, Oregon, America) techniques, and chemical composition clearly recorded by energy dispersive X-ray spectrometer (EDS) tests. In order to ensure the quality of the picture, the sample was sputtered with a thin Au-Pt. Surface area analysis was conducted on an ASAP2020HD88 instrument (Micromeritics Instrument Corporation, Shanghai, China) based on the Brunauer–Emmett–Teller (BET) theory. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) curves, and electrochemical impedance spectroscopy (EIS) measurements were examined using a three-electrode system on CHI 660E electrochemical station (Chenhua, Shanghai, China) in 6 M KOH. The sample was used as the working electrode, a platinum foil (2 cm \times 2 cm), and a saturated calomel electrode as the counter and

the reference electrode, respectively. The mass loading of the active material on the Ni foam was about 4 mg, which was determined by weighing the Ni foam substrate before and after applying the active material. And the specific capacitance of the single electrode was calculated using the equation:

$$C = i\Delta t / (S\Delta V) \tag{1}$$

$$C = i\Delta t / (m\Delta V) \tag{2}$$

where *C* is the specific capacitance, *i* is the discharge current, Δt is the discharge time, *S* and *m* are assigned as the area and mass of the electrode material, and ΔV represents the potential window.



Figure 1. Schematic illustration of synthesis process for NZO-12h.

The electrochemical performance of asymmetric supercapacitor was examined in a two-electrode system. The NZO-12h sample was used as the positive electrode and activated carbon as the negative electrode, which was separated by a piece non-woven fabric. Further, a negative electrode was prepared using activated carbon and polytetrafluoroethylene (PTFE) with mass ratio of 9:1. After, homogeneous slurry was formed through continuous mixing, and then obtained slurry was spread on cleaned Ni foam. Next, the Ni foam was dried at 340 K for 6 h in a vacuum oven.

The mass loading of positive and negative electrode was calculated according to the following equation:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+} \tag{3}$$

where *m* (g) represents the mass loading, *C* is specific capacitance, and ΔE is potential window, respectively, of positive (+) and negative (–) electrodes.

3. Results

The XRD measurement was used to analyze phase information of the NZO-12h electrode, and the result is displayed in Figure 2. Three strong peaks can be found at 44.51°, 51.84°, and 76.41°, which corresponds to (110), (200), and (220) diffraction of Ni (JCPDS 65-2865). There were two diffraction peaks which matched well with the (100) and (101) planes of ZnO (JCPDS 36-1451). The characteristic peak at 43.01° corresponds to the (200) planes of NiO (JCPDS 47-1049). The XRD pattern indicates two phases of NiO and ZnO could be indexed in the hybrid. Therefore, NZO was successfully fabricated using the hydrothermal method.

The chemical composition and oxidation state of the samples were evaluated by XPS measurements. The fitted spectra were obtained by Gaussian simulation method, as shown in Figure 3. The Ni $2p_{3/2}$ main peak was located at 855.4 eV and its satellite peak at 861.1 eV, while the Ni $2p_{1/2}$

main peak was centered at 873.8 eV and its satellite peak at 879.9 eV, respectively (Figure 3a). The result, which is consistent with the previously reported values, further confirms that NiO can be detected in as-prepared samples [28]. In the Figure 3b, it is clear that the prominent peaks of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ appear at 1021.2 eV and 1044.5 eV, which was attributed to Zn²⁺ in the sample [29]. In the O 1s region, there are three peaks, as shown in Figure 3c. Two peaks can be found at 527.9 eV and 530.5 eV, which represents O²⁻ (Ni) and O²⁻ (Zn), respectively. In addition, a pronounced peak was observed at 532.8 eV, which corresponds to H₂O [28]. These results clearly determine the formation of ZnO and NiO in this sample.



Figure 3. X-ray photoelectron spectroscopy (XPS) survey spectra of NZO-12h: (**a**) Ni 2p; (**b**) Zn 2p; (**c**) O 1s.

Figure 4 exhibits the SEM images at different magnifications of NZO-3h (Figure 4a–c), NZO-6h (Figure 4d–f), NZO-12h (Figure 4g–i), and NZO-24h (Figure 4j–l), respectively. From low-magnification SEM images (Figure 4a,d,g,j), it can be found that NZO materials grow on the Ni foam, and present

the corresponding structure and its distribution states. For the NZO-3h sample, it exhibits a nanosheet structure with an average diameter of 720 nm. Besides, the edge of these nanosheets has a jagged structure, which can be observed from a high magnification of Figure 4b,c. For NZO-6h, the as-prepared sample was composed of nanosheets with an average diameter of 540 nm, and these nanosheets form a flower-like structure. Notably, the center of the flower-like structure has a large accumulation of nanosheets, which affects the electrochemical conductivity of the electrode material. For the NZO-12h sample, it can be seen that a 3D sphere was made up of intertwined nanosheets, and the nanosheets were supported by each other, forming a flower-like structure. The diameter of nanosheets was about 610 nm. Moreover, there were a few pores in these nanosheets, as shown in Figure 4i, which facilitates the diffusion of electroactive species. Such unique porous structure provides numerous pathways for effective active sites electron/ion transport, which also accelerates the occurrence of redox reactions. Thus, the NZO-12h sample has excellent electrochemical performance. Obviously, when the reaction time is 24 h, the structure of the sample is still close to the flower-like; however, it is different from other electrode materials. The magnified image (Figure 41) illustrates NZO-24h was composed of many short-rods and nanosheets.



Figure 4. FESEM images of (a-c) NZO-3h; (d-f) NZO-6h; (g-i) NZO-12h; and (j-l) NZO-24h.

EDS is an important technique to examine and analyze elemental component of samples. EDS was performed at a working distance of 15 mm and an acceleration voltage of 15 kV. The typical EDS spectrum of the NZO-12h sample is shown in Figure 5. It can be clearly seen that Ni, O, and Zn were detected in the as-obtained sample, which is consistent with the XPS result.



Figure 5. Typical EDS spectrum of the NZO-12h.

To observe the detailed structural characteristic of the NZO-12h sample, TEM and highresolution-TEM (HRTEM) were carried out, as shown in Figure 6. Further, TEM can be used to distinguish between crystalline and amorphous structures. Meanwhile, precise information about the surface morphology can be provided. The low-magnification TEM image is exhibited in Figure 6a, which reveals the existence of interdigitated nanosheets for NZO-12h. The result coincided with the corresponding SEM patterns. The HRTEM of the NZO-12h sample is displayed in Figure 6b–d, and the images show that there are two kinds of diffraction fringes with the lattice spacing of about 0.237 nm and 0.241 nm, which can be ascribed to the (111) planes of NiO and (101) planes of ZnO. The diffraction spots in the selected area electron diffraction (SAED) pattern suggest crystallization property of the as-prepared sample is unsatisfactory. Therefore, the conclusion could be made undoubtedly that the flower-like NZO sample has been successfully prepared using the hydrothermal method.



Figure 6. TEM characterization of NZO-12h: (**a**) TEM image; (**b**–**d**) high-resolution-TEM images; inset in (**c**,**d**) are corresponding selected area electron diffraction (SAED) images of ZnO and NiO.

The nitrogen adsorption and desorption test was used to analyze the porous structure, and the result is displayed in Figure 7. The flower-like NZO-12h sample exhibits a high Brunauer–Emmett–Teller (BET) surface area of 20.3350 cm²/g, which is beneficial for the transport and diffusion of electrolyte. The pore size distribution of NZO-12h is shown in Figure 7b, and an average pore diameter of 2 nm was obtained by the Barret-Joyner-Halenda (BJH) method using the adsorption branch of the isotherm. From this feature, it can be concluded that the NZO-12h sample has micropores. Consequently, the NZO-12h sample has good electrochemical performance.



Figure 7. Nitrogen adsorption and desorption isotherms and pore size distribution of NZO-12h.

To explore the effect of structure on performance, a series of electrochemical tests of NZO materials were performed. The CV curves of NZO electrodes (3 h, 6 h, 12 h, and 24 h) were measured at 5 mV/s within potential windows of 0–0.5 V, and the results are presented in Figure 8a. Obviously, well-defined anodic and cathodic peaks of each curve can be observed. The special shape reflects the pseudocapacitive characteristics of the NZO, which is different from the CV curves of the double-layer capacitor [30]. Clearly, it can be found NZO-12h exhibits the largest enclosed area, implying its specific capacitance is better than that of NZO-3h, NZO-6h, and NZO-24h electrodes. As is known, electrochemical performance is related to the structure of samples. From these images it clearly shows that the morphology of NZO-24h is different from NZO-12h, which consists of short-rods and sheets. However, intertwined nanosheets of flower-like NZO-12h create a number of pores that have a large effect on increasing the capacitance of the electrode material. In Figure 8a, NZO-3h and NZO-6h samples exhibit almost the same double layer electrochemical surface area. The enclosed area is smaller when the reaction time is 6 h, which is caused by poor electrical conductivity. Inconsistent redox peak position change trend is mainly caused by the difference of pore structure. Figure 8b describes the CV curves of the NZO-12h at different scan rates (5, 10, 25, and 50 mV/s). As the scan rates increases, the distance between redox peaks becomes wide due to polarization. Moreover, the CV shape is similar at different scan rates, which means that the electrode material has good reversibility [31], as shown in the inset of Figure 8b. Therefore, it is necessary to further investigate the electrochemical properties of the NZO-12h.

The GCD tests of different NZO electrodes were conducted at a current density of 5 mA/cm², as shown in Figure 9a. The area specific capacitances of the NZO-3h, NZO-6h, NZO-12h, and NZO-24h were 1.49 F/cm², 0.41 F/cm², 3.94 F/cm², and 3.32 F/cm². Meanwhile, the mass specific capacitances of these materials were measured to be 372.5 F/g, 102.5 F/g, 985.0 F/g, and 830.0 F/g. It can be clearly found that the NZO-12h electrode has the highest specific capacitance, which is in agreement with the CV result. The electrochemical performance of NZO-12h is better than NZO-3h, 6h, and 24h, which was mainly attributed to its unique structural characteristics. Further, when the hydrothermal reaction is 12 h, more active material grows on Ni foam. And its approximate flower-like structure also promotes the contact between sample and electrolyte, thereby exhibiting better performance.

The relationship between specific capacitances and hydrothermal time is shown in Figure 9b. It can be found the NZO-12h exhibits higher specific capacitance than others.



Figure 8. (a) CV curves of NZO electrodes prepared using different hydrothermal times at a scan rate of 5 mV/s; (b) rate performance curves of the NZO-12 h electrode, the insets show the i_p vs. Vplots of the corresponding CV curves.



Figure 9. (a) GCD curves at a current density of 5 mA/cm² for NZO electrodes with different hydrothermal times; (b) the specific capacitances of the NZO with different hydrothermal times; (c) GCD curves of the NZO-12h electrode at different current densities; (d) rate capacitance calculation of the NZO-12h electrode.

Figure 9c shows the GCD curves of the NZO-12h electrode at different current densities. Clearly, there exists a discharge platform for each non-linear GCD curve. Actually, redox reaction is commonly associated with pseudocapacitive charge/discharge process. When the current density is 5 mA/cm², the GCD curve has the longest discharge time. Rate capacitance calculation of NZO-12h derived

from Figure 9c is shown in Figure 9d, and area specific capacitances are 3.94, 3.41, 3.02, 2.69, 2.51, and 2.35 F/cm² at the current density of 5, 10, 20, 30, 40, and 50 mA/cm², respectively. According to Equation (2), the mass specific capacitances of 985.0 F/g, 852.5 F/g, 755 F/g, 673.1 F/g, 627.5 F/g, and 587.5 F/g were obtained at the same current density, respectively. In addition, NZO-12h maintains 59.6% of the maximum capacitance at 50 mA/cm², highlighting its excellent rate capability. As expected, NZO-12h has better electrochemical performance than previous reports. In detail, specific capacitances of different electrode materials are shown in Table 1. The high specific capacitance was attributed to the unique structure of NZO-12h. Further, the large specific surface area of such a flower-like structure allows the electrode material to have more active sites, which is significant to the performance of itself. Thus, the flower-like NZO-12h has the potential to meet the demand of supercapacitor applications.

Table 1. Spe	ecific capacita	nces of differen	t electrode	materials.
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Material	Structure	Specific Capacitance	Reference
NiO@PC	Hierarchical structure	$57 \text{ mF/cm}^2 \text{ at } 5 \text{ mA/cm}^2$	[32]
NiO@C@Cu2O hybrid	Core-shell heterostructure	$2.18 \text{ F/cm}^2 \text{ at } 1 \text{ mA/cm}^2$	[33]
HNCS-NiO	Hierarchical structure	$880.6 \text{ mF/cm}^2 \text{ at } 0.8 \text{ mA/cm}^2$	[34]
NiO/MnO ₂	Heterostructure	286 mF/cm ² at 0.5 mA/cm ²	[35]
ZnO/MnO ₂ @carbon cloth	Core-shell structure	$138.7 \text{ mF/cm}^2 \text{ at } 1 \text{ mA/cm}^2$	[36]
NiO/Ni(OH) ₂ /PEDOT	Nanoflower structure	$404.1 \text{ mF/cm}^2 \text{ at } 4 \text{ mA/cm}^2$	[37]
NZO-12h	Flower-like structure	$3.94 \text{ F/cm}^2 \text{ at } 5 \text{ mA/cm}^2$	Our work

Long stability is an important parameter to determine whether the as-prepared material can be effectively applied in supercapacitors, and the result is shown in Figure 10. After 1500 cycles, 74.9% capacitance remained, indicating its high cycling stability. The GCD curves for first seven and last seven cycles are shown in Figure 10b,c. It can be found that the shape of the curves is similar, meaning that there is no significant structural change.



Figure 10. (**a**) 1500 cycle performance of the NZO-12h at a current density of 20 mA/cm²; (**b**) first 7 cycles of NZO-12h; (**c**) final 7 cycles of NZO-12h.

To further understand the electrochemical behavior, the EIS plots of the NZO with different hydrothermal times were collected between 0.01 Hz and 10 kHz, as shown in Figure 11a. Generally speaking, the EIS curve includes a linear portion of the low-frequency region and a non-linear portion of the high-frequency region. For the electrode material, its stability properties, conductivity, and charge–discharge rate [38] are better when the equivalent series resistance (R_s) value is smaller. The diameter of a semicircle at high-frequency represents charge–transfer resistance R_{ct} . The slope of the line can be ascribed to the diffusion and kinetics process called the Warburg impedance (Z_w). Importantly, a steep line indicates the better capacitive behavior in low-frequency region. Thus, NZO-6h is unable to be a promising electrode material. However, the R_s values of the three samples (NZO-3h, NZO-12h, and NZO-24h) are particularly close, being 0.35 Ω , 0.31 Ω , and 0.33 Ω . R_{ct} values are 3.39 Ω , 1.25 Ω , and 1.74 Ω , respectively. It can be concluded that NZO-12h has the smallest R_s and R_{ct} . Moreover, the slope of the NZO-12h is closer to the vertical line, representing a more rapid ion-diffusion-transfer rate. Therefore, NZO-12h is an excellent candidate for the supercapacitor, which is consistent with above analysis.



Figure 11. (a) EIS plots of NZO electrodes with different hydrothermal time; (b) the corresponding high-frequency region of EIS.

In order to explore practical applications of the flower-like NZO-12h, it is necessary to fabricate an asymmetric capacitor. The NZO-12h was regarded as a positive electrode and AC as a negative electrode, and the electrochemical performance was tested in 6 M KOH electrolyte. After calculation, the mass ratio of the NZO-12h and AC was 1:3.98. Figure 12a shows the CV curves of AC at different scan rates in the potential window of -1.0-0 V. It was found that the shape of the curve was close to a rectangle without redox peak, indicating the behavior of an electrical double-layer capacitance. When the scan rate increases from 5 to 50 mV/s, the capacitance of the AC remains 73.4%, indicating its good rate capability. Figure 12b shows the CV curves of AC and NZO-12h, which was recorded in a three-electrode system and tested at a scan rate of 10 mV/s. There is no doubt that the positive and negative electrodes were well matched each other for assembling asymmetric supercapacitors. Figure 12c exhibits the CV curves of the asymmetric supercapacitor at different scan rates of 5, 10, 25, and 50 mV/s with the potential of 0-1.5 V. It was found that the shape of the CV curves were nearly quasi-rectangular, even at a scan rate of 50 mV/s, indicating the asymmetric capacitor device has low resistance. The GCD curves of the asymmetric supercapacitor at different current densities were shown in Figure 12d. According to GCD measurement, energy density (E) and power density (P) can be calculated as follows [39]:

$$E = \frac{1}{2 \times 3.6} C V^2 \tag{4}$$

$$P = E \times 3600 / \Delta t \tag{5}$$



Figure 12. (a) CV curve of AC at different scan rates; (b) CV curve of AC and NZO-12h separately tested in a three-electrode system at 10 mV/s; (c) CV curve of asymmetric supercapacitor at different scan rates; (d) GCD curve of asymmetric supercapacitor at different current density; (e) Ragone plots of asymmetric supercapacitor.

In this equation, *E* (Wh kg⁻¹) and *P* (W kg⁻¹) are the energy density and power density. *C*, *V*, and Δt are specific capacitance, operating voltage, and discharge time, respectively.

Ragone plot relative to the corresponding energy and power densities of the asymmetric supercapacitor was shown in Figure 12e. Clearly, the highest energy density of 27.13 Wh kg⁻¹ was obtained at a power density of 321.42 W kg⁻¹, and still remains 14.81 Wh kg⁻¹ at a high-power density of 744.72 W kg⁻¹. The obtained values are superior to results found in the literature of other asymmetric systems, such as fabricated CNFs/MnO₂//AC (20.3 Wh kg⁻¹ at 485 W kg⁻¹) [40], MnO₂//AC (7.8 Wh kg⁻¹ at 338 W kg⁻¹) [41], the novel CNT@NCT@MnO₂ composites (13.3 Wh kg⁻¹ at 90 W kg⁻¹) [42], FeCo₂O₄@MnO₂ nanostructures on carbon fibers (22.68 Wh kg⁻¹ at 406.01 W kg⁻¹) [43],

graphene- $MnO_2//graphene-MnO_2$ (6.8 Wh kg⁻¹, 62.0 W kg⁻¹) [44], and AC//MnO₂-CNTs (13.3 Wh kg⁻¹ at 600.0 W kg⁻¹) [45].

4. Conclusions

In summary, NZO with various hydrothermal time was fabricated through a facile, simple, and low-cost hydrothermal method. For four kinds of electrode materials, the NZO-12h exhibited better electrochemical performance than the others (NZO-3h, NZO-6h, and NZO-24h). This phenomenon was attributed to the large specific surface area of the NZO-12h sample, which is advantageous for the occurrence of redox reactions. Electrochemical results show the NZO-12h electrode exhibited a high specific capacitance of 985.0 F/g (3.94 F/cm^2) at 5 mA/cm² and 587.5 F/g (2.35 F/cm^2) at 50 mA/cm². Besides, 74.9% capacitance retention was obtained after 1500 cycles charge/discharge cycles, which indicates excellent cycling stability of NZO-12h. Moreover, the electrochemical performance of an asymmetric supercapacitor was measured, and the specific capacitance of the device was 85.7 F/g at 0.4 A/g. Moreover, the device can deliver a maximum energy density of 27.13 Wh kg⁻¹ at a power density of 321.42 W kg⁻¹. Therefore, the obtained NZO-12h hybrid is a promising candidate for asupercapacitor. Importantly, our present study provides a strategy for the preparation of other hybrid metal oxides.

Author Contributions: S.N. conceived and designed the experiments; Z.X. fabricated and R.Z. characterized the sample; K.C. and Z.X. collaborated in XRD and SEM measurement; J.Z., P.Y., and X.W. analyzed the data. All authors discussed the experiment results and contributed to writing the paper.

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