



Article

CoNiO₂/Co₃O₄ Nanosheets on Boron Doped Diamond for Supercapacitor Electrodes

Zheng Cui ¹, Tianyi Wang ¹, Ziyi Geng ¹, Linfeng Wan ¹, Yaofeng Liu ¹, Siyu Xu ¹, Nan Gao ^{1,*}, Hongdong Li ^{1,*} and Min Yang ^{2,*}

¹ State Key Lab of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China; cui Zheng21@mails.jlu.edu.cn (Z.C.); w850308519@163.com (T.W.); ziyigeng2021@163.com (Z.G.); wanlf20@mails.jlu.edu.cn (L.W.); lyf21@mails.jlu.edu.cn (Y.L.); xusy21@mails.jlu.edu.cn (S.X.)

² Sichuan Provincial Key Laboratory for Structural Optimization and Application of Functional Molecules, College of Chemistry and Life Science, Chengdu Normal University, Chengdu 611130, China

* Correspondence: gaon@jlu.edu.cn (N.G.); hldli@jlu.edu.cn (H.L.); yangmin820525@126.com (M.Y.)

Abstract: Developing novel supercapacitor electrodes with high energy density and good cycle stability has aroused great interest. Herein, the vertically aligned CoNiO₂/Co₃O₄ nanosheet arrays anchored on boron doped diamond (BDD) films are designed and fabricated by a simple one-step electrodeposition method. The CoNiO₂/Co₃O₄/BDD electrode possesses a large specific capacitance (214 mF cm⁻²) and a long-term capacitance retention (85.9% after 10,000 cycles), which is attributed to the unique two-dimensional nanosheet architecture, high conductivity of CoNiO₂/Co₃O₄ and the wide potential window of diamond. Nanosheet materials with an ultrathin thickness can decrease the diffusion length of ions, increase the contact area with electrolyte, as well as improve active material utilization, which leads to an enhanced electrochemical performance. Additionally, CoNiO₂/Co₃O₄/BDD is fabricated as the positive electrode with activated carbon as the negative electrode, this assembled asymmetric supercapacitor exhibits an energy density of 7.5 W h kg⁻¹ at a power density of 330.5 W kg⁻¹ and capacity retention rate of 97.4% after 10,000 cycles in 6 M KOH. This work would provide insights into the design of advanced electrode materials for high-performance supercapacitors.

Keywords: BDD substrate; CoNiO₂/Co₃O₄; electrodeposition; supercapacitor electrodes



Citation: Cui, Z.; Wang, T.; Geng, Z.; Wan, L.; Liu, Y.; Xu, S.; Gao, N.; Li, H.; Yang, M. CoNiO₂/Co₃O₄ Nanosheets on Boron Doped Diamond for Supercapacitor Electrodes. *Nanomaterials* **2024**, *14*, 474. <https://doi.org/10.3390/nano14050474>

Academic Editor: Fabrizio Pirri

Received: 17 February 2024

Revised: 28 February 2024

Accepted: 2 March 2024

Published: 5 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Due to the increasingly serious problems of air pollution and insufficient resource storage, the development of clean and sustainable energy storage devices is highly pursued. As a kind of electrochemical energy storage device, supercapacitors have advantages of high power density, fast charging and discharging speed, and long cycle life [1,2]. In general, the electrode material is one of determinant factors affecting the performance of supercapacitors, such as capacity and cycling stability in the reaction [3]. According to the energy storage mechanism, the boundary between capacitive behavior (capacitive) and battery behavior (faradaic) is relatively clear: capacitive is physical energy storage, faradaic is chemical energy storage [4]. The difference is whether there is a transition between electrical energy and chemical energy. In other words, whether there is a redox reaction [5]. The electrode materials are classified into electrical double-layer capacitors and pseudocapacitors [5,6]. For electrical double-layer capacitors, carbonaceous materials are usually used as the electrode, which accumulates charge at the electrode-electrolyte interface through reversible ion adsorption under electrostatic interaction [4,7]. On the other hand, pseudocapacitors derive their capacitance from the various available oxidation states for rapid surface or near-surface redox charge transfer [8], transition metal oxides and binary transition metal molybdates are considered as electrode materials for pseudocapacitors because of their high specific capacitance and energy density [9,10]. Improving the energy

density of supercapacitors is crucial to meet future practical applications without sacrificing the power density.

Transition metal oxide material Co_3O_4 has received widespread attentions as supercapacitor electrodes due to its high theoretical specific capacitance (3560 F g^{-1}), low price, environmental friendliness and chemical durability [11,12]. Nevertheless, its poor conductivity limits the transport of electrolyte ions, resulting in a slow electrochemical process of charge storage and delivery [12]. The method of combining a pseudocapacitive material with high conductivity as a framework [13] could effectively increase the utilization of active materials and result in higher capacitance. Due to the redox reaction of nickel and cobalt ions being more abundant than that of a single component of nickel oxide or cobalt oxide ($\text{Co}^{2+/3+}$ and $\text{Ni}^{2+/3+}$) [14], CoNiO_2 has higher electrical conductivity and superior electrochemical activity [15]. We suppose that the Co_3O_4 and CoNiO_2 composite structure would have high electrochemical performance.

However, note that both Co_3O_4 and CoNiO_2 -based electrodes have low working voltage windows, typically smaller than 0.6 V (Table S1). The low energy density of supercapacitors is mainly attributed to relatively low voltage window and specific capacity. Based on the formulation: $E = 1/2CV^2$, the energy density (E) linearly increases with specific capacitance (C) and square of maximum operation voltage (V) [16]. Hence, the improvement of maximum operation voltage and specific capacitance is an effective route to increase the specific energy. This strategy has been successfully applied in a hierarchical $\text{Co}_3\text{O}_4/\text{MnO}_2$ composite material [17]. With the rapid development of chemical vapor deposition methods and the optimization of production processes, the current cost of boron-doped diamond (BDD) is gradually decreasing, so it has a high market value [18]. BDD emerges as a promising electrode material due to high stability in many corrosive media [19,20], low background current and wide potential window in aqueous solution ($\sim 3.2 \text{ V}$) [21,22]. The most noticeable effect related to the sp^3/sp^2 ratio on BDD is the variation on the potential window. The sp^2 -bonded carbon playing a modulator role in charge-transfer approaches promoting outer-shell or inner-sphere electron-transfer mechanisms, can effectively capture transport electrons to restrain oxygen evolution at high voltage region, and then construct a supernal potential window [21]. Previously, Jiang et al. [23] used a mesh diamond as an electrode and obtained an energy density of $0.016 \text{ W h kg}^{-1}$ and a power density of 9.54 W kg^{-1} . Yang et al. [24] reported diamond nanoneedle composite graphite as an electrode, an energy density of $0.013 \text{ W h kg}^{-1}$ and the power density of 12.79 W kg^{-1} were obtained. Therefore, BDD is chosen as a substrate to enlarge the potential window of a $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ composite structure, thus the electrochemical performance should be further improved.

Herein, we provide a new strategy for synthesizing $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ nanosheet arrays on BDD ($\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$) through the simple electrodeposition process. The $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ sample as a supercapacitor electrode provides high specific capacitance of 214 mF cm^{-2} and long-term cycling stability (85.9% after 10,000 cycles). In addition, an asymmetric supercapacitor is assembled using $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ and activated carbon as the positive and negative electrodes. This work provides strategic insights for the rational design of supercapacitor electrodes with high areal capacitance and large window voltage.

2. Materials and Methods

2.1. Synthesis of BDD

BDD samples were synthesized on silicon substrate (Tianjin Jingchen Electronics Company, Tianjin, China) by microwave plasma chemical vapor deposition (MPCVD). Nucleation of the silicon substrate was carried out by suspension containing nanodiamond particles (5–10 nm, Tianjin Qianyu Superhard Technology Co., Ltd., Tianjin, China). First, a small amount of nano-diamond was added on the sandpaper, and ground on the polishing Si surface for half an hour to make even scratches on the surface. Then, the polished Si sheet is put into a mixed solution of acetone and alcohol containing nano-diamond

powder for more than half an hour of ultrasound. The nano-diamond impinges on the Si substrate surface through ultrasound to form a micro impact crater, which can reduce the nucleation barrier and increase the nucleation density when growing the diamond. Finally, the samples were ultrasonically cleaned with alcohol and deionized water for 5 min to remove the residual diamond powder on the surface, and then placed on the sample holder to dry. In this way, the nano-diamond was successfully fixed on the silicon substrate. With the ratio of gaseous methane (CH_4) and hydrogen (H_2) 5% as the reaction source, under the condition of microwave power of 2200 W and process pressure of 10 kPa, boron source trimethyl borate ($\text{C}_3\text{H}_9\text{BO}_3$) was introduced using H_2 . The substrate was heated to about 850 °C using an induction heater, and the substrate temperature was measured using a thermocouple. After deposition for 12 h, the thickness of BDD film was about 20 μm . The mass of hydrogen consumed to obtain a BDD film with a thickness of 20 μm was 25.63 g. According to the test of Hall effector, the conductivity of BDD was 113.63 S cm^{-1} .

2.2. Synthesis of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$

$\text{CoNiO}_2/\text{Co}_3\text{O}_4$ arrays were conducted on BDD by using a CHI 760E model Electrochemical Workstation in a standard three-electrode system. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8 mmol) and NH_4Cl (8 mmol) were mixed in 80 mL deionized water and transferred into 100 mL electrolytic cell. With BDD as the working electrode, Pt sheet as the counter electrode and Ag/AgCl electrode as the reference electrode, a three-electrode system of potentiostatic electrodeposition was constructed. The effect of NiCo precursor on 1000 s, 2500 s, and 5000 s reaction time was investigated at constant voltage of -1.0 V. Finally, the $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ hybrid structure was obtained by annealing for 2 h at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in an argon atmosphere at 300 °C.

2.3. Materials Characterization

The morphology of the samples was investigated with a scanning electron microscope (SEM, FEI Magellan 400, Hillsboro, OR, USA). Transmission electron microscopy (TEM, JEOL JEM-2100FS, Tokyo, Japan) and energy-dispersive X-ray spectroscopy (EDS) were used to study the microstructures. X-ray photoelectron spectroscopy (XPS) analysis was performed with the VGESCALAB MK II system (Uppsala, Sweden) using a monochromatic AlK α (1486.6 eV) X-ray source under ultra-high vacuum (background pressure: 4.4×10^{-9} mBar). The crystalline phases of the samples were determined using X-ray diffractometer (XRD, SmartLab, Rigaku, Tokyo, Japan). The average thickness of samples was estimated by atomic force microscopy (AFM, Cypder ES, Oxford, UK). Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) of the prepared $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ electrode were performed on CHI760E electrochemical workstation (Chenhua, Shanghai, China).

2.4. Negative Electrode Preparation and Assembly of Asymmetrical Supercapacitor

The negative electrode was prepared by mixing activated carbon (specific surface area: $1800\text{ m}^2\text{ g}^{-1}$, granularity: 5–8 μm) purchased from Aladdin Industrial Corporation (Shanghai, China), acetylene black (conductive additive), and polyvinylidene fluoride (PVDF) binder in ethyl alcohol solvent with a weight ratio of 8:1:1. The slurry was then coated onto a nickel foam current collector (Suzhou Kesheng and metal Materials Co., Ltd., Suzhou, China) ($1\text{ cm} \times 1\text{ cm}$) and dried for 24 h under a vacuum at 80 °C. The two-electrode structure of an asymmetric supercapacitor assembled with $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ electrode, activated carbon as negative electrode and separator (NKK-MPF30AC-100, Tokyo, Japan) was tested in 6 M KOH solution (Aladdin Industrial Corporation, Pico Rivera, CA, USA). Figure S1 shows the supercapacitor structure diagram. The mass ratio of two electrodes was balanced by the relationship:

$$m_+/m_- = (C_- \times \Delta E_-)/(C_+ \times \Delta E_+) \quad (1)$$

where m (g) was the mass of the electrode materials (anode or cathode), C (F/g) was the specific capacitance, and ΔE was the potential window.

3. Results

The synthesized BDD film is composed of dense grains with uniform grain size, and the grains are free of cracks and holes (Figure 1a). Figure 1b–d shows the SEM images of annealed $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ composites with deposition time of 1000 s, 2500 s and 5000 s, respectively. The thickness of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ nanosheet can be accurately measured by AFM. The vertical coordinate represents the roughness of the sample, and the horizontal coordinate represents the thickness of the sample. After 1000 s of deposition, a crisscrossing skeleton structure is found (Figure 1b). Layer thickness of roughly is 10 nm by AFM analysis (Figure S2a). Figure 1c shows that the vertically arranged $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ nanosheets grow dense, when the reaction deposition time is 2500 s. As shown in Figure S2b, the thickness of the nanosheet structure is about 20 nm. The heterostructure consisting of two vertically aligned interconnected hierarchical nanosheets not only provide a large surface area and an efficient diffusion pathway for fast electron/ion transport, but also generate abundant electron-altering heterointerface, resulting in a synergistic effect between the two components [25]. When the reaction proceeds further to 5000 s, the morphology of $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ is obviously agglomerated, exhibiting a pronounced massive structure (Figure 1d).

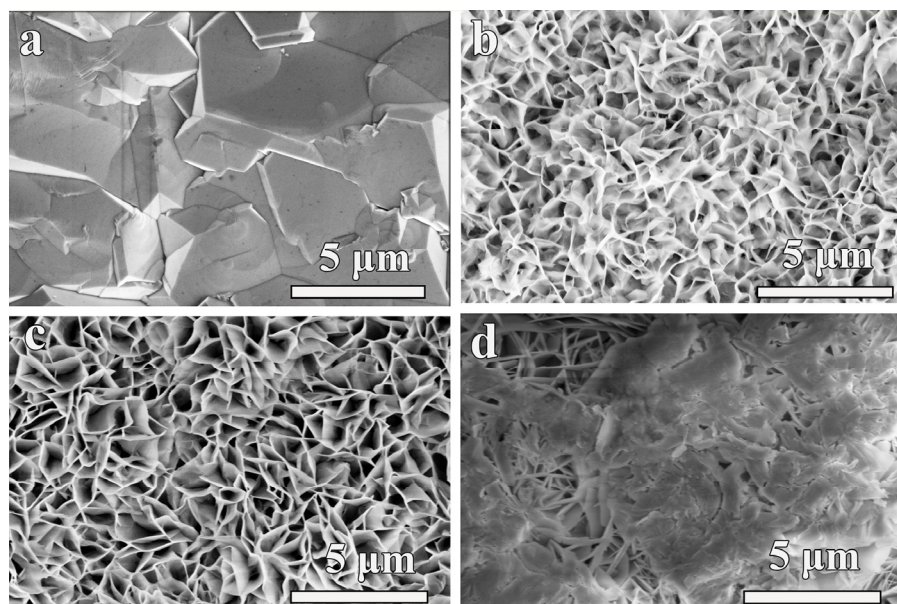


Figure 1. SEM images of (a) pristine BDD film, $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ at deposition time of (b) 1000 s, (c) 2500 s, and (d) 5000 s.

Since thicker and denser structures are beneficial to improve structural stability and ion transport efficiency during the reaction process [26,27], thus we suppose that the $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ structure with deposition time of 2500 s has the best electrochemical performance. To confirm this conclusion, CV, GCD and EIS results of electrodes with reaction times of 1000 s, 2500 s and 5000 s in Figure S3 demonstrate that the sample with reaction time of 2500 s has the largest CV area, longest discharge time and lowest diffusion resistance. Thus, the $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ sample with deposition time of 2500 s is used in the following.

To further characterize the structure of the synthesized sample, Figure 2 shows TEM image, high-resolution TEM image (HRTEM) and corresponding EDS mapping analysis results of $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ powder scraped from BDD substrate. $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ displays a typical two-dimensional nanosheet morphology with a smooth surface, and the measured layer spacing is 94 nm (Figure 2a). Proper layer spacing is conducive to ion embedding [8].

In HRTEM image (Figure 2b), the interplanar spacings of 0.122 nm and 0.202 nm are indexed to the CoNiO_2 (222) and Co_3O_4 (400) planes, respectively, indicating the coexistence of CoNiO_2 and Co_3O_4 in the composite. Moreover, the EDS elemental mapping images in Figure 2c verify the presence of O, Ni and Co elements in the samples, further proving the successful synthesis of CoNiO_2 and Co_3O_4 heterostructures. Atomic ratio from EDS data is listed in Table S2.

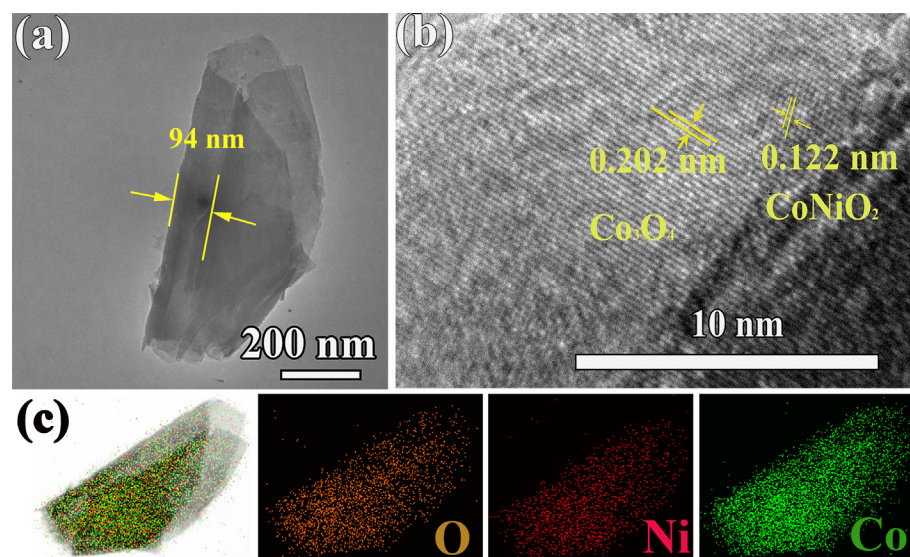


Figure 2. (a) TEM image, (b) HRTEM image, and (c) TEM-EDS elemental mapping images of $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ powder scraped from BDD substrate.

Figure 3a displays the XRD pattern of $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ powder scraped from BDD substrate. The characteristic peaks are located at 36.8° , 42.8° , 61.7° and 73.9° , which are indexed to (111), (200), (220) and (311) planes of CoNiO_2 (JCPDS No. 10-0188). Furthermore, the diffraction peaks at 19.0° , 31.2° , 36.8° , 38.5° , 44.8° , 49.1° , 55.6° , 59.3° , 65.2° , 68.6° , 69.7° and 74.1° correspond to (111), (220), (311), (222), (400), (331), (422), (511), (440), (531), (442) and (620) planes of Co_3O_4 (JCPDS No. 43-1003). The more detailed elemental composition and the oxidation state of the prepared $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ are further characterized by XPS measurements and the corresponding results are presented in Figure 3b–d. Binding energy is calibrated by fixing the saturated hydrocarbon component of the C1s peak at 284.8 eV [28]. Gaussian function fitting is performed for all peaks [29]. The Co 2p $^{3/2}$ and Co 2p $^{1/2}$ spectra can be fitted to two spin-orbit doublets of Co^{2+} and Co^{3+} . The Co^{2+} peaks are centered at binding energies of 798.7 and 782.8 eV, and the other peaks at 781.0 and 796.8 eV are attributed from Co^{3+} [30]. These results confirm that the Co species have $\text{Co}^{2+}/\text{Co}^{3+}$ in the hybrid electrodes. In Figure 3c, the Ni 2p spectra display Ni 2p $^{3/2}$ and Ni 2p $^{1/2}$ with two shakeup satellites. In addition, the peaks of Ni 2p $^{3/2}$ and Ni 2p $^{1/2}$ can be broadened by several peaks, whose binding energies center at 855.1, 856.2, 872.4 and 873.6 eV [31], indicating the coexistence of Ni^{2+} and Ni^{3+} in hybrid electrodes. The O 1s spectrum in Figure 3d has two obvious peaks at 532.2 eV and 531.3 eV, which represents metal-oxygen bonds and surface physically adsorbed water, respectively [32]. Thus, the sample surface is mainly composed of Ni^{2+} , Ni^{3+} , Co^{3+} , Co^{2+} and O^{2-} ions, which provides abundant faraday reaction sites and is beneficial to achieve excellent electrochemical performance [32,33]. In addition, we provide XPS of BDD films in Figure S4. BDD has a small amount of sp^2 carbon, which is conducive to improve the conductivity of the electrode.

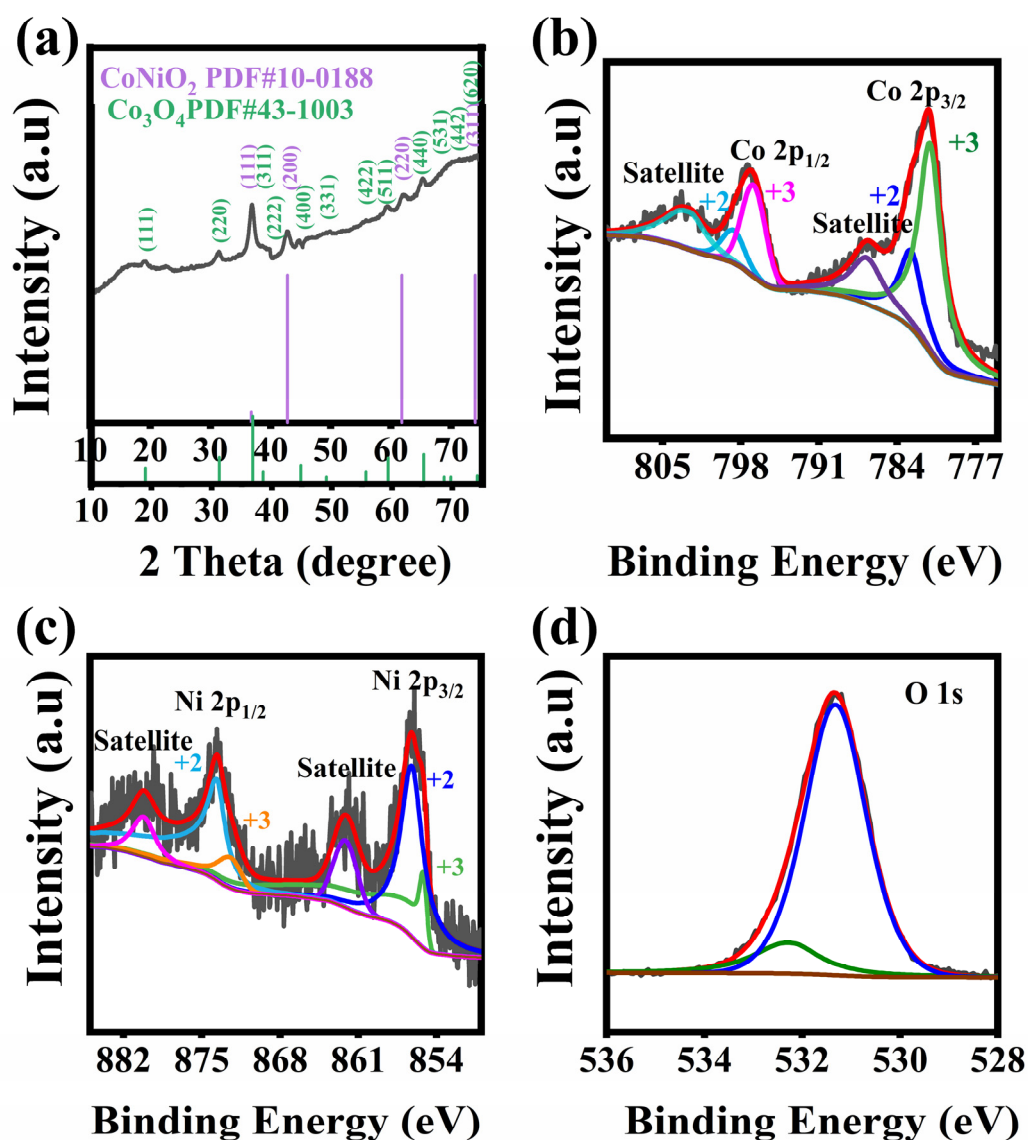


Figure 3. (a) XRD pattern and XPS spectra of (b) Ni 2p, (c) Co 2p, (d) O 1s for CoNiO₂/Co₃O₄ powder scraped from the BDD substrate.

In order to highlight the advantages of CoNiO₂/Co₃O₄/BDD electrode, CV, GCD and EIS curves of pristine BDD and CoNiO₂/Co₃O₄/BDD electrodes are presented in Figure 4a–c. The CV curves are performed at a scan rate of 5 mV s^{−1} in 1 M Na₂SO₄ electrolyte in Figure 4a. CoNiO₂/Co₃O₄/BDD show a pair of relative symmetrical redox peaks in the voltage window range of 0–1.2 V, indicating faradaic reactions occurred during CV process and good reversibility [34]. It is attributed to the reversible redox reaction of Co and Ni (Co^{2+/3+} and Ni^{2+/3+}) and correspond to the CV peaks of CoNiO₂/Co₃O₄/BDD, which would further increase the capacitance. BDD shows a rectangular CV curve, indicating the double layer capacitance process of CV [6]. It is also shown that the enclosed area of CV for CoNiO₂/Co₃O₄/BDD is larger than that of BDD, suggesting the higher electrochemical capacity of CoNiO₂/Co₃O₄/BDD. The capacities of CoNiO₂/Co₃O₄/BDD and BDD are evaluated by GCD analysis at 1 mA cm^{−2} in Figure 4b. The GCD of BDD has an almost symmetrical linear shape, indicating the typical behavior of an ideal electrical double layer capacitor [35]. The GCD of CoNiO₂/Co₃O₄/BDD has two distinct potential plateaus, confirming that faradaic reduction reactions occur during GCD process [36]. The GCD results match well with the CV results. In addition, the

discharge time of CoNiO₂/Co₃O₄/BDD (257 s) is much longer than that of BDD (0.7 s), denoting the higher specific capacity of CoNiO₂/Co₃O₄/BDD.

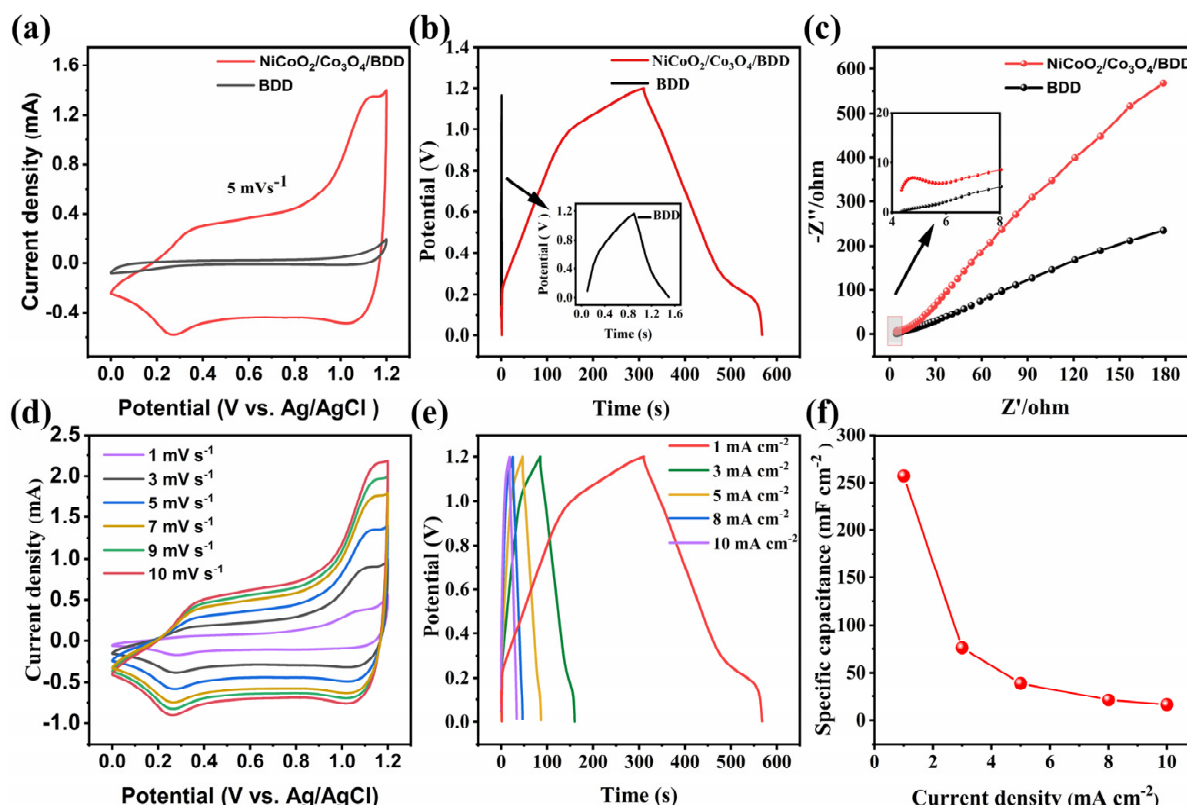


Figure 4. (a) CV curves at a scanning rate of 50 mV s⁻¹, (b) GCD curves at a scanning rate of 1 mA cm⁻², and (c) Nyquist plots of BDD and CoNiO₂/Co₃O₄/BDD electrodes and equivalent circuit. (d) CV, (e) GCD, (f) specific capacitances of CoNiO₂/Co₃O₄/BDD electrode.

EIS measurements are performed at open circuit potential in the frequency range of 0.01–100 kHz using a 6 M KOH electrolyte in Figure 4c. The CoNiO₂/Co₃O₄/BDD electrode shows linear in the Nyquist plot, indicating that the active material is completely dispersed in the electrolyte, which further confirms that the CoNiO₂/Co₃O₄/BDD electrode has ideal rate capability [14]. In addition, improving the wettability is an effective method to improve their capacitive performance [37]. As shown in Figure S5, CoNiO₂/Co₃O₄/BDD structure (42°) has a smaller hydrophilic angle than pristine BDD (94°), due to its unique layer structure and better wetting ability in the electrolyte.

Figure 4d shows the CV curves of CoNiO₂/Co₃O₄/BDD at various scan rates. The response current increases linearly with the increase of scan rate. The lower the scanning rate, the better the CV symmetry, the closer to the double layer mechanism, and the better the reversibility [34]. In particular, CoNiO₂/Co₃O₄/BDD extends the voltage window to 1.2 V, which is larger than that of CoNiO₂ and Co₃O₄ based pseudocapacitive electrodes (Table S1), due to the high potential window of diamond substrate [15,25,38]. The GCD curves in Figure 4e exhibit a symmetrical shape over a wide current density range of 1 to 10 mA cm⁻², revealing high coulombic efficiency and electrochemical capacitive characteristics due to the highly reversible redox reactions of CoNiO₂/Co₃O₄/BDD electrode during charge-discharge process. The area specific capacitance C_s (μF cm⁻²) is calculated from the GCD curves according to equation [39]:

$$C_s = \frac{i \times \Delta t}{s \times \Delta V} \quad (2)$$

where i (A) is the current rate of charge and discharge, Δt (s) is the discharge time, s (cm^2) is the effective area of the electrode, and ΔV (V) is the voltage window. Then the specific capacitance value of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ is largest (214 mF cm^{-2}) at the current density of 1 mA cm^{-2} (Figure 4f), being larger than that for $\text{Co}_3\text{O}_4/\text{BDD}$ (124 mF cm^{-2}) in Figure S6. Notably, the specific capacitance of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ exceeds most diamond-based supercapacitors (Table S3) [18]. In addition, the electrode achieves superior cycling stability, a capacity retention of 85.9% and coulombic efficiency of 99.3% are obtained after 10,000 cycles (Figure S7). The percentages of the capacitive and diffusion contributions can be further quantified by the following Equation (3):

$$i(v) = k_1 v + k_2 v^{1/2} \quad (3)$$

where k_1 and k_2 are arbitrary constants, and $k_1 v$ and $k_2 v^{1/2}$ correspond to capacitive processes and diffusion-controlled effects, respectively. At a scan rate of 1.0 mV s^{-1} , the capacitive contribution is 48%, and the diffusion-controlled process accounts for 52% (Figure S8a). As shown in Figure S8, with the increase in the scan rate, the capacitive contribution is even higher. This suggests that the capacitive contribution plays a dominant role in the total capacity, and a faraday redox reaction occurs mainly on the surfaces of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ nanostructures.

Finally, to verify the energy storage performance of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ electrode in practical application, an asymmetric supercapacitor device is assembled using $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ as the positive electrode and activated carbon as the negative electrode. The CV curves in Figure 5a show the mixed capacity of the electric double-layer capacitor and pseudocapacitance. When the scan rate increases, the area of CV curve enlarges, and the peak shape has good symmetry (Figure 5b), indicating a high coulombic efficiency and good reversibility for the fast charge/discharge process. As shown in Figure 5c, the specific capacitance is largest (79.1 mF cm^{-2} at 2 A cm^{-1}), and the corresponding mass specific capacitance is presented in Figure S9. Furthermore, the almost symmetrical GCD curves indicate high coulombic efficiency and electrochemical reversibility. As shown in Figure 5d, after 10,000 cycles, the device maintains 97.4% specific capacity and coulombic efficiency of 90.8%. In the process of cycling, electrolyte ions have deep adsorption and intercalation in the layer, which changes the structure and leads to the degradation of the electrode structure. At the same time, impurities in the electrode or electrolyte may cause side reactions and affect the stability of the cycle [40]. The energy density E (Wh kg^{-1}) and power density P (kW kg^{-1}) of the device are calculated by Equations (4) and (5), respectively [11]

$$E = \frac{1}{2} C_g \Delta V^2 \quad (4)$$

$$P = \frac{E}{\Delta t} \quad (5)$$

where C_g (F g^{-1}) is the specific capacitance. Ragone for energy storage devices is intuitive and meaningful [41]. Figure S10 also summarizes the energy and power densities of other diamond electrode materials available in the literature. The $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ device can deliver a maximum energy density of 7.5 W h kg^{-1} at 330.5 W kg^{-1} , and 1.2 W h kg^{-1} at 1098.1 W kg^{-1} (Figure S10). This value is higher than graphite@NDD/graphite@NDD (NDD, nano-needles diamond) [23], BDD/BDD [35] and porous BDD/porous BDD [42]. A red light-emitting diode is lit directly by only one asymmetrical supercapacitor without any other power assistance, indicating that this electrode material has excellent application prospects.

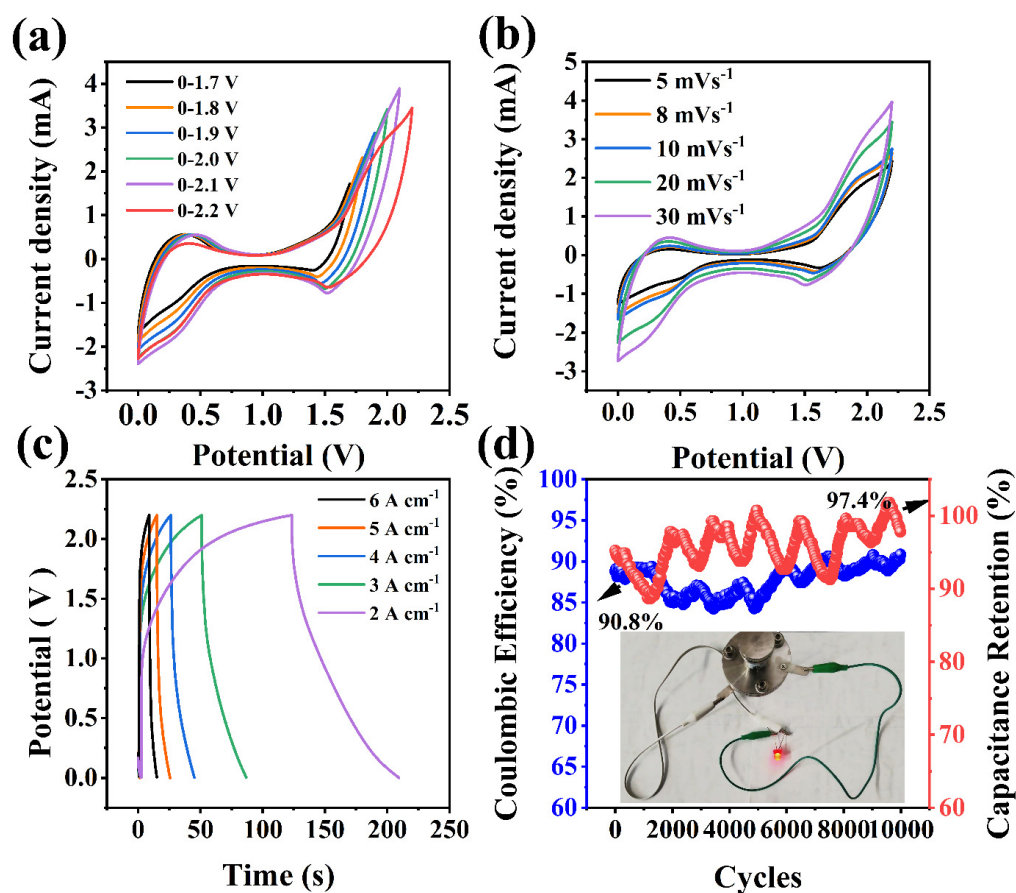


Figure 5. (a) CV curves at various voltage ranges (20 mV s^{-1}), (b) CV curves at various scan rates, (c) GCD curves at different current densities, (d) cycling stability of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ at 5 mA cm^{-2} for asymmetric supercapacitor device using $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ as the positive electrode and AC as the negative electrode. Inset is photograph of a red light-emitting diode lit for several minutes with a cell device.

4. Conclusions

In summary, $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ nanosheet arrays are synthesized on BDD with the enhanced electrochemical performance by one-step electrodeposition strategy, and used for supercapacitor electrodes. The surface morphology of $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ can be controlled by the deposition time, and an optimum deposition time is 2500 s. The $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ electrode shows an excellent capacitance value of 214 mF cm^{-2} along with a voltage window of 1.2 V. In addition, the electrode achieves superior cycling performance stability (a capacity retention of 85.9% after 10,000 cycles). Finally, the assembled symmetric supercapacitors device with $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ as the positive electrode has an energy density of 7.5 W h kg^{-1} , when the power density is 330.5 W kg^{-1} , and the capacitance maintains 97.4% of the initial value after 10,000 cycles. The improvement in electrochemical performance is attributed to $\text{CoNiO}_2/\text{Co}_3\text{O}_4$ with unique two-dimensional nanosheet structure, improved electrical conductivity and BDD with a wide voltage window.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano14050474/s1>. Figure S1: Supercapacitor structure diagram. Figure S2: $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ at deposition time of (a) 1000 s, (b) 2500 s the images obtained by AFM image and the corresponding thickness distribution histogram. Figure S3: (a) CV, (b) GCD curves and (c) EIS curves of $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ samples with reaction times of 1000 s, 2500 s and 5000 s. Figure S4: XPS of BDD films. Figure S5: Contact angle measurement of (a) pristine BDD and (b) $\text{CoNiO}_2/\text{Co}_3\text{O}_4/\text{BDD}$ with $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ electrolyte solution. Figure S6: GCD curves at a scanning rate of 2 mA cm^{-2} of $\text{Co}_3\text{O}_4/\text{BDD}$ electrode. Figure S7: Cycling stability of

CoNiO₂/Co₃O₄/BDD at 2 mA cm^{−2}. Figure S8: (a) Capacitive and diffusion-controlled charge storage contributions at the scan rate of 1.0 mV s^{−1} (b) The contribution ratio of capacitive and diffusion-controlled charge storage at various scan rates ranging from 1 to 3 mV s^{−1} for CoNiO₂/Co₃O₄/BDD electrode. Figure S9: GCD curves at a current density of 0.3 to 1 A g^{−1} of the CoNiO₂/Co₃O₄/BDD electrode. Figure S10: Ragone plot of energy density and power density of CoNiO₂/Co₃O₄/BDD and other electrodes obtained from the literature; Table S1: Electrochemical property parameters of Co₃O₄ and CoNi-based electrodes for supercapacitors; Table S2: Co/Ni ratio from EDS data; Table S3: Capacitance of diamond-based electrodes for supercapacitors. References [35,43–61] are cited in the Supplementary Materials.

Author Contributions: Conceptualization, H.L.; formal analysis, Z.C., T.W., Z.G., L.W., Y.L., S.X., N.G., M.Y. and H.L.; data curation, Z.C. and M.Y.; writing—original draft preparation, Z.C. and N.G.; writing—review and editing, N.G. and H.L.; funding acquisition, H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (NSFC) (Grant No. 52172044) and Program of Science and Technology Development Plan of Jilin Province of China (No. 20230201151 GX).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Lin, T.; Chen, I.W.; Liu, F.; Yang, C.; Bi, H.; Xu, F.; Huang, F. Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage. *Science* **2015**, *350*, 1508. [\[CrossRef\]](#)
- Huang, J.; Xie, Y.; You, Y.; Yuan, J.; Xu, Q.; Xie, H.; Chen, Y. Rational Design of Electrode Materials for Advanced Supercapacitors: From Lab Research to Commercialization. *Adv. Funct. Mater.* **2023**, *33*, 2213095. [\[CrossRef\]](#)
- Zhong, M.; Zhang, M.; Li, X. Carbon nanomaterials and their composites for supercapacitors. *Carbon Energy* **2022**, *4*, 950–985. [\[CrossRef\]](#)
- Chen, S.; Qiu, L.; Cheng, H.-M. Carbon-Based Fibers for Advanced Electrochemical Energy Storage Devices. *Chem. Rev.* **2020**, *120*, 2811–2878. [\[CrossRef\]](#)
- Wang, F.; Wu, X.; Yuan, X.; Liu, Z.; Zhang, Y.; Fu, L.; Zhu, Y.; Zhou, Q.; Wu, Y.; Huang, W. Latest advances in supercapacitors: From new electrode materials to novel device designs. *Chem. Soc. Rev.* **2017**, *46*, 6816–6854. [\[CrossRef\]](#)
- Yan, J.; Li, S.; Lan, B.; Wu, Y.; Lee, P.S. Rational Design of Nanostructured Electrode Materials toward Multifunctional Supercapacitors. *Adv. Funct. Mater.* **2019**, *30*, 1902564. [\[CrossRef\]](#)
- Zhai, Z.; Zhang, L.; Du, T.; Ren, B.; Xu, Y.; Wang, S.; Miao, J.; Liu, Z. A review of carbon materials for supercapacitors. *Mater. Des.* **2022**, *221*, 111017. [\[CrossRef\]](#)
- Kang, J.; Zhang, S.; Zhang, Z. Three-Dimensional Binder-Free Nanoarchitectures for Advanced Pseudocapacitors. *Adv. Mater.* **2017**, *29*, 1700515. [\[CrossRef\]](#) [\[PubMed\]](#)
- Liu, Y.; Wang, N.; Yang, C.; Hu, W. Sol–gel synthesis of nanoporous NiCo₂O₄ thin films on ITO glass as high-performance supercapacitor electrodes. *Ceram. Int.* **2016**, *42*, 11411–11416. [\[CrossRef\]](#)
- Senthilkumar, B.; Vijaya Sankar, K.; Kalai Selvan, R.; Danielle, M.; Manickam, M. Nano α-NiMoO₄ as a new electrode for electrochemical supercapacitors. *RSC Adv.* **2013**, *3*, 352–357. [\[CrossRef\]](#)
- Liang, R.; Du, Y.; Xiao, P.; Cheng, J.; Yuan, S.; Chen, Y.; Yuan, J.; Chen, J. Transition Metal Oxide Electrode Materials for Supercapacitors: A Review of Recent Developments. *Nanomaterials* **2021**, *11*, 1248. [\[CrossRef\]](#)
- Liu, R.; Zhou, A.; Zhang, X.; Mu, J.; Che, H.; Wang, Y.; Wang, T.-T.; Zhang, Z.; Kou, Z. Fundamentals, advances and challenges of transition metal compounds-based supercapacitors. *Chem. Eng. J.* **2021**, *412*, 128611. [\[CrossRef\]](#)
- Li, P.; Li, J.; Zhao, Z.; Fang, Z.; Yang, M.; Yuan, Z.; Zhang, Y.; Zhang, Q.; Hong, W.; Chen, X.; et al. A General Electrode Design Strategy for Flexible Fiber Micro-Pseudocapacitors Combining Ultrahigh Energy and Power Delivery. *Adv. Sci.* **2017**, *4*, 1700003. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhang, J.; Chen, Z.; Wang, Y.; Li, H. Morphology-controllable synthesis of 3D CoNiO₂ nano-networks as a high-performance positive electrode material for supercapacitors. *Energy* **2016**, *113*, 943–948. [\[CrossRef\]](#)
- Li, Y.; Han, X.; Yi, T.; He, Y.; Li, X. Review and prospect of NiCo₂O₄-based composite materials for supercapacitor electrodes. *J. Energy Chem.* **2019**, *31*, 54–78. [\[CrossRef\]](#)
- Pohlmann, S.; Balducci, A. A new conducting salt for high voltage propylene carbonate-based electrochemical double layer capacitors. *Electrochim. Acta* **2013**, *110*, 221–227. [\[CrossRef\]](#)
- Liu, G.; Kang, C.; Fang, J.; Fu, L.; Zhou, H.; Liu, Q. MnO₂ nanosheet-coated Co₃O₄ complex for 1.4 V extra-high voltage supercapacitors electrode material. *J. Power Sources* **2019**, *431*, 48–54. [\[CrossRef\]](#)

18. Yu, S.; Yang, N.; Liu, S.; Jiang, X. Diamond supercapacitors: Progress and perspectives. *Curr. Opin. Solid State Mater. Sci.* **2021**, *25*, 100922. [[CrossRef](#)]
19. Banerjee, D.; Sankaran, K.J.; Deshmukh, S.; Ficek, M.; Yeh, C.-J.; Ryl, J.; Lin, I.N.; Bogdanowicz, R.; Kanjilal, A.; Haenen, K.; et al. Single-step grown boron doped nanocrystalline diamond-carbon nanogress hybrid as an efficient supercapacitor electrode. *Nanoscale* **2020**, *12*, 10117–10126. [[CrossRef](#)]
20. Yu, S.; Yang, N.; Vogel, M.; Mandal, S.; Williams, O.A.; Jiang, S.; Schönherr, H.; Yang, B.; Jiang, X. Battery-like Supercapacitors from Vertically Aligned Carbon Nanofiber Coated Diamond: Design and Demonstrator. *Adv. Energy Mater.* **2018**, *8*, 1702947. [[CrossRef](#)]
21. Garcia-Segura, S.; Vieira dos Santos, E.; Martínez-Huitle, C.A. Role of sp^3/sp^2 ratio on the electrocatalytic properties of boron-doped diamond electrodes: A mini review. *Electrochem. Commun.* **2015**, *59*, 52–55. [[CrossRef](#)]
22. Mei, R.; Wei, Q.; Zhu, C.; Ye, W.; Zhou, B.; Ma, L.; Yu, Z.; Zhou, K. 3D macroporous boron-doped diamond electrode with interconnected liquid flow channels: A high-efficiency electrochemical degradation of RB-19 dye wastewater under low current. *Appl. Catal. B* **2019**, *245*, 420–427. [[CrossRef](#)]
23. Yu, S.; Sankaran, K.J.; Korneychuk, S.; Verbeeck, J.; Haenen, K.; Jiang, X.; Yang, N. High-performance supercapacitors using graphite@diamond nano-needle capacitor electrodes and redox electrolytes. *Nanoscale* **2019**, *11*, 17939–17946. [[CrossRef](#)] [[PubMed](#)]
24. Yu, S.; Yang, N.; Zhuang, H.; Mandal, S.; Williams, O.A.; Yang, B.; Huang, N.; Jiang, X. Battery-like supercapacitors from diamond networks and water-soluble redox electrolytes. *J. Mater. Chem. A* **2017**, *5*, 1778–1785. [[CrossRef](#)]
25. Li, X.; Ren, J.; Sridhar, D.; Xu, B.B.; Algadi, H.; El-Bahy, Z.M.; Ma, Y.; Li, T.; Guo, Z. Progress of layered double hydroxide-based materials for supercapacitors. *Mater. Chem. Front.* **2023**, *7*, 1520–1561. [[CrossRef](#)]
26. Verma, S.; Arya, S.; Gupta, V.; Mahajan, S.; Furukawa, H.; Khosla, A. Performance analysis, challenges and future perspectives of nickel based nanostructured electrodes for electrochemical supercapacitors. *J. Mater. Res. Technol.* **2021**, *11*, 564–599. [[CrossRef](#)]
27. Qi, D.; Liu, Y.; Liu, Z.; Zhang, L.; Chen, X. Design of Architectures and Materials in In-Plane Micro-supercapacitors: Current Status and Future Challenges. *Adv. Mater.* **2016**, *29*, 1602802. [[CrossRef](#)] [[PubMed](#)]
28. Boryakov, A.V.; Surodin, S.I.; Kryukov, R.N.; Nikolichev, D.E.; Zubkov, S.Y. Spectral fit refinement in XPS analysis technique and its practical applications. *J. Electron. Spectrosc. Relat. Phenom.* **2018**, *229*, 132–140. [[CrossRef](#)]
29. Biesinger, M.C.; Payne, B.P.; Grosvenor, A.P.; Lau, L.W.M.; Gerson, A.R.; Smart, R.S.C. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* **2011**, *257*, 2717–2730. [[CrossRef](#)]
30. Jia, H.; Wang, Z.; Zheng, X.; Lin, J.; Liang, H.; Cai, Y.; Qi, J.; Cao, J.; Feng, J.; Fei, W. Interlaced Ni-Co LDH nanosheets wrapped Co₉S₈ nanotube with hierarchical structure toward high performance supercapacitors. *Chem. Eng. J.* **2018**, *351*, 348–355. [[CrossRef](#)]
31. Fang, G.; Ji, X.; Shi, H.; Zhang, C.; Guo, Z.; Tang, T.; Liu, W. Constructing built-in electric field in 3D core-shell p-n heterostructure of NiFe-LDH nanosheets modified Cr-doped Ni₃S₂ nanofibers for efficient and stable oxygen evolution reaction. *J. Alloys Compd.* **2024**, *970*, 172583. [[CrossRef](#)]
32. He, W.; Liang, Z.; Ji, K.; Sun, Q.; Zhai, T.; Xu, X. Hierarchical Ni-Co-S@Ni-W-O core-shell nanosheet arrays on nickel foam for high-performance asymmetric supercapacitors. *Nano Res.* **2018**, *11*, 1415–1425. [[CrossRef](#)]
33. Chang, L.; Chen, S.; Fei, Y.; Stacchiola, D.J.; Hu, Y.H. Superstructured NiMoO₄@CoMoO₄ core-shell nanofibers for supercapacitors with ultrahigh areal capacitance. *Proc. Natl. Acad. Sci. USA* **2023**, *120*, e2219950120. [[CrossRef](#)]
34. Minakshi, M.; Wickramaarachchi, K. Electrochemical aspects of supercapacitors in perspective: From electrochemical configurations to electrode materials processing. *Prog. Solid State Chem.* **2023**, *69*, 100390. [[CrossRef](#)]
35. Wang, J.; He, Z.; Tan, X.; Wang, T.; Liu, L.; He, X.; Liu, X.D.; Zhang, L.; Du, K. High-performance 2.6 V aqueous symmetric supercapacitor based on porous boron-doped diamond via regrowth of diamond nanoparticles. *Carbon* **2020**, *160*, 71–79. [[CrossRef](#)]
36. Gan, Z.; Yin, J.; Xu, X.; Cheng, Y.; Yu, T. Nanostructure and Advanced Energy Storage: Elaborate Material Designs Lead to High-Rate Pseudocapacitive Ion Storage. *ACS Nano* **2022**, *16*, 5131–5152. [[CrossRef](#)]
37. Chen, Y.; Jiang, Y.; Liu, Z.; Yang, L.; Du, Q.; Zhuo, K. Hierarchical porous N-doped graphene aerogel with good wettability for high-performance ionic liquid-based supercapacitors. *Electrochim. Acta* **2021**, *366*, 137414. [[CrossRef](#)]
38. Ray, P.K.; Mohanty, R.; Parida, K. Recent advancements of NiCo LDH and graphene based nanohybrids for supercapacitor application. *J. Energy Storage* **2023**, *72*, 108335. [[CrossRef](#)]
39. Li, H.; Wang, J.; Chu, Q.; Wang, Z.; Zhang, F.; Wang, S. Theoretical and experimental specific capacitance of polyaniline in sulfuric acid. *J. Power Sources* **2009**, *190*, 578–586. [[CrossRef](#)]
40. Fleischmann, S.; Mitchell, J.B.; Wang, R.; Zhan, C.; Jiang, D.-e.; Presser, V.; Augustyn, V. Pseudocapacitance: From Fundamental Understanding to High Power Energy Storage Materials. *Chem. Rev.* **2020**, *120*, 6738–6782. [[CrossRef](#)]
41. Temesgen, T.; Bekele, E.T.; Gonfa, B.A.; Tufa, L.T.; Sabir, F.K.; Tadesse, S.; Dessie, Y. Advancements in biomass derived porous carbon materials and their surface influence effect on electrode electrochemical performance for sustainable supercapacitors: A review. *J. Energy Storage* **2023**, *73*, 109293. [[CrossRef](#)]
42. Wang, J.; He, Z.; Tan, X.; Wang, T.; He, X.; Zhang, L.; Huang, J.; Chen, G.; Du, K. Hybrid supercapacitors from porous boron-doped diamond with watersoluble redox electrolyte. *Surf. Coat. Technol.* **2020**, *398*, 126103. [[CrossRef](#)]
43. Pallavolu, M.R.; Kumar, Y.A.; Mani, G.; Nallapureddy, R.R.; Parvathala, A.; Albaqami, M.D.; Karami, A.M.; Joo, S.W. A novel hybridized needle-like Co₃O₄/N-CNO composite for superior energy storage asymmetric supercapacitors. *J. Alloys Compd.* **2022**, *908*, 164447. [[CrossRef](#)]
44. Pan, X.; Chen, X.; Li, Y.; Yu, Z. Facile Synthesis of Co₃O₄ Nanosheets Electrode with Ultrahigh Specific Capacitance for Electrochemical Supercapacitors. *Electrochim. Acta* **2015**, *182*, 1101–1106. [[CrossRef](#)]

45. Liu, S.; Kang, L.; Hu, J.; Jung, E.; Zhang, J.; Jun, S.C.; Yamauchi, Y. Unlocking the Potential of Oxygen-Deficient Copper-Doped Co_3O_4 Nanocrystals Confined in Carbon as an Advanced Electrode for Flexible Solid-State Supercapacitors. *ACS Energy Lett.* **2021**, *6*, 3011–3019. [\[CrossRef\]](#)
46. Lai, C.; Guo, Y.; Zhao, H.; Song, H.; Qu, X.; Huang, M.; Hong, S.W.; Lee, K. High-performance double “ion-buffering reservoirs” of asymmetric supercapacitors enabled by battery-type hierarchical porous sandwich-like Co_3O_4 and 3D graphene aerogels. *Adv. Compos. Hybrid Mater.* **2022**, *5*, 2557–2574. [\[CrossRef\]](#)
47. Umeshbabu, E.; Rajeshkhanna, G.; Ranga Rao, G. Effect of solvents on the morphology of NiCo_2O_4 /graphene nanostructures for electrochemical pseudocapacitor application. *J. Solid State Electrochem.* **2015**, *20*, 1837–1844. [\[CrossRef\]](#)
48. Yang, J.; Li, H.; He, S.; Du, H.; Liu, K.; Zhang, C.; Jiang, S. Facile Electrodeposition of NiCo_2O_4 Nanosheets on Porous Carbonized Wood for Wood-Derived Asymmetric Supercapacitors. *Polymers* **2022**, *14*, 2521. [\[CrossRef\]](#)
49. Hu, X.; Wan, C.; Meng, X.; Tang, A.; Ju, X. Porous NiCoO_2 nanospheres encapsulated in nitrogen-doped carbon shell achieving high energy storage for aqueous supercapacitors and zinc-ion batteries. *Appl. Surf. Sci.* **2022**, *582*, 152456. [\[CrossRef\]](#)
50. Liu, B.; Hou, J.; Zhang, T.; Xu, C.; Liu, H. A three-dimensional multilevel nanoporous NiCoO_2/Ni hybrid for highly reversible electrochemical energy storage. *J. Mater. Chem. A* **2019**, *7*, 16222–16230. [\[CrossRef\]](#)
51. Wang, X.; Fang, Y.; Shi, B.; Huang, F.; Rong, F.; Que, R. Three-dimensional $\text{NiCo}_2\text{O}_4@/\text{NiCo}_2\text{O}_4$ core-shell nanocones arrays for high-performance supercapacitors. *Chem. Eng. J.* **2018**, *344*, 311–319. [\[CrossRef\]](#)
52. Wang, X.W.; Wang, X.E.; Liu, Y.P.; Kong, Y.Y.; Sun, L.Y.; Hu, Y.C.; Zhu, Q.Q. Hydrothermal process fabrication of $\text{NiO-NiCoO}_2\text{-Co}_3\text{O}_4$ composites used as supercapacitor materials. *J. Mater. Sci. Mater. Electron.* **2017**, *28*, 14928–14934.
53. Yu, S.; Yang, N.; Zhuang, H.; Meyer, J.; Mandal, S.; Williams, O.A.; Lilge, I.; Schönherr, H.; Jiang, X. Electrochemical Supercapacitors from Diamond. *J. Phys. Chem. C* **2015**, *119*, 18918–18926. [\[CrossRef\]](#)
54. Gao, F.; Nebel, C.E. Diamond nanowire forest decorated with nickel hydroxide as a pseudocapacitive material for fast charging–discharging. *Phys. Status Solidi (a)* **2015**, *212*, 2533–2538. [\[CrossRef\]](#)
55. Zhang, J.; Yu, X.; Zhao, Z.-y.; Zhang, Z.; Li, J. Influence of pore size of Ti substrate on structural and capacitive properties of Ti/boron doped diamond electrode. *J. Alloys Compd.* **2019**, *777*, 84–93. [\[CrossRef\]](#)
56. Lu, Z.; Huang, N.; Zhai, Z.; Chen, B.; Liu, L.; Song, H.; Yuan, Z.; Zhang, C.; Yang, B.; Jiang, X. Integration of 3D interconnected porous microstructure and high electrochemical property for boron-doped diamond by facile strategy. *J. Mater. Sci. Technol.* **2022**, *105*, 26–35.
57. Shi, C.; Li, C.; Li, M.; Li, H.; Dai, W.; Wu, Y.; Yang, B. Fabrication of porous boron-doped diamond electrodes by catalytic etching under hydrogen–argon plasma. *Appl. Surf. Sci.* **2016**, *360*, 315–322. [\[CrossRef\]](#)
58. Guo, T.; Yang, N.; Yang, B.; Schulte, A.; Jin, Q.; Koch, U.; Mandal, S.; Engelhard, C.; Williams, O.A.; Schönherr, H.; et al. Electrochemistry of nitrogen and boron Bi-element incorporated diamond films. *Carbon* **2021**, *178*, 19–25. [\[CrossRef\]](#)
59. Xu, J.; Yang, N.; Heuser, S.; Yu, S.; Schulte, A.; Schönherr, H.; Jiang, X. Achieving Ultrahigh Energy Densities of Supercapacitors with Porous Titanium Carbide/Boron-Doped Diamond Composite Electrodes. *Adv. Energy Mater.* **2019**, *9*, 1803623. [\[CrossRef\]](#)
60. Zhang, J.; Zhao, Z.; Zhang, Z.; Guo, L.; Xu, L.; Sun, P.; Wang, M.; Gao, M.; Li, Y.; Li, D.; et al. Construction of flexible fiber-shaped boron-doped diamond film and its supercapacitor application. *J. Colloid Interface Sci.* **2023**, *629*, 813–821. [\[CrossRef\]](#)
61. Zhang, J.; Yu, X.; Zhang, Z.-Q.; Zhao, Z.-Y. Preparation of boron-doped diamond foam film for supercapacitor applications. *Appl. Surf. Sci.* **2020**, *506*, 144645. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.