

Hybrid Composite Ni(OH)₂@NiCo₂O₄ Grown on Carbon Fiber Paper for High-Performance Supercapacitors

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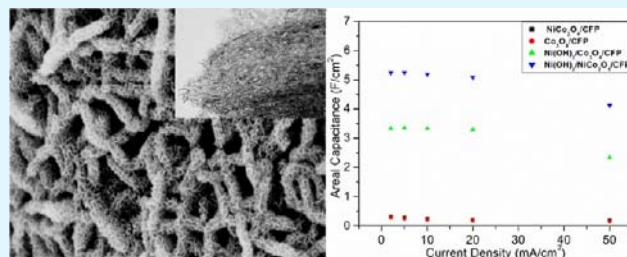
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S Supporting Information

ABSTRACT: We have successfully fabricated and tested the electrochemical performance of supercapacitor electrodes consisting of Ni(OH)₂ nanosheets coated on NiCo₂O₄ nanosheets grown on carbon fiber paper (CFP) current collectors. When the NiCo₂O₄ nanosheets are replaced by Co₃O₄ nanosheets, however, the energy and power density as well as the rate capability of the electrodes are significantly reduced, most likely due to the lower conductivity of Co₃O₄ than that of NiCo₂O₄. The 3D hybrid composite Ni(OH)₂/NiCo₂O₄/CFP electrodes demonstrate a high areal capacitance of 5.2 F/cm² at a cycling current density of 2 mA/cm², with a capacitance retention of 79% as the cycling current density was increased from 2 to 50 mA/cm². The remarkable performance of these hybrid composite electrodes implies that supercapacitors based on them have potential for many practical applications.

KEYWORDS: energy storage, supercapacitor, carbon fiber, cobalt oxide, hybrid, composite



Electrical energy storage and conversion systems play a vital role in efficient and cost-effective utilization of clean energy from renewable sources.^{1–3} In particular, electrochemical energy storage and conversion devices such as batteries, fuel cells, and supercapacitors are considered the most promising candidate for portable and mobile applications.⁴ Among them, supercapacitors offer a number of advantages over conventional batteries, including fast charge rate, long-term cycling stability, and the ability to deliver up to ten times more power. These features are desirable for a range of applications, from electric vehicles to smart grids.^{5–10} Pseudocapacitors (with reversible Faradaic redox reactions at the electrode surfaces) usually offer much higher specific capacitance than supercapacitors made of carbonaceous materials based on double-layer charge storage.^{11–14} Transition metal oxides and hydroxides are the most popular materials for the electrodes of pseudoapacitors because of their high theoretical capacitance, low cost, and low toxicity.^{15–18} However, the experimentally obtainable values are often much lower than the theoretical expectations, especially when operated at high cycling rate, while the conductivity of the electrodes may be limited.

Recently three-dimensional (3D) hybrid electrodes have been used for pseudocapacitors. With large surface area and short diffusion path for electrons and ions, 3D hybrid structures are well-suited architectures for high-performance supercapacitor electrodes.^{11,19–23} Here, we report a binder-free hybrid composite electrode with nanoarchitecture Ni(OH)₂/NiCo₂O₄ directly grown on carbon fiber paper (CFP). Comparing with a similar

structure such as NiCo₂O₄ sheets and Ni(OH)₂/CoO walls on a metal substrate, our hybrid composite Ni(OH)₂/NiCo₂O₄/CFP could offer superior capacity and rate capability.^{16,20}

The hybrid composite electrode was prepared by a facile two-step method. First, NiCo₂O₄ nanosheets were grown on CFP using an electrodeposition process followed annealing at 300 °C for 2 h.¹⁶ Then, another layer of Ni(OH)₂ was grown on the NiCo₂O₄ sheets by a second electrodeposition process, as described in the Supporting Information. The uniform morphology of the NiCo₂O₄ nanosheets grown on CFP is shown in Figure 1a. The TEM image illustrates that the NiCo₂O₄ sheets are a porous structure composed of 10–20 nm nanocrystallites with pores 2–4 nm in diameter. (Figure 1b, Figure S1 in the Supporting Information) The HRTEM and SAED show the poly crystalline phase of these sheets with the thickness of several nanometers. (Figure 1c, d) After the second growth of Ni(OH)₂, the ultrathin sheets were converted to thick walls, as illustrated in Figure 1e. As can be seen from the Figure 1f, the Ni(OH)₂ layer on the surface of NiCo₂O₄ is also constructed by small ultrathin sheets. The X-ray diffraction pattern shows that the hybrid structure contains cubic NiCo₂O₄ with a space group of *Fd3m* (JCPDS Card No.73-1702) and α -Ni(OH)₂ phase (38–0715) (see Figure S4 in the Supporting Information). This 3D hybrid composite Ni(OH)₂/NiCo₂O₄ on

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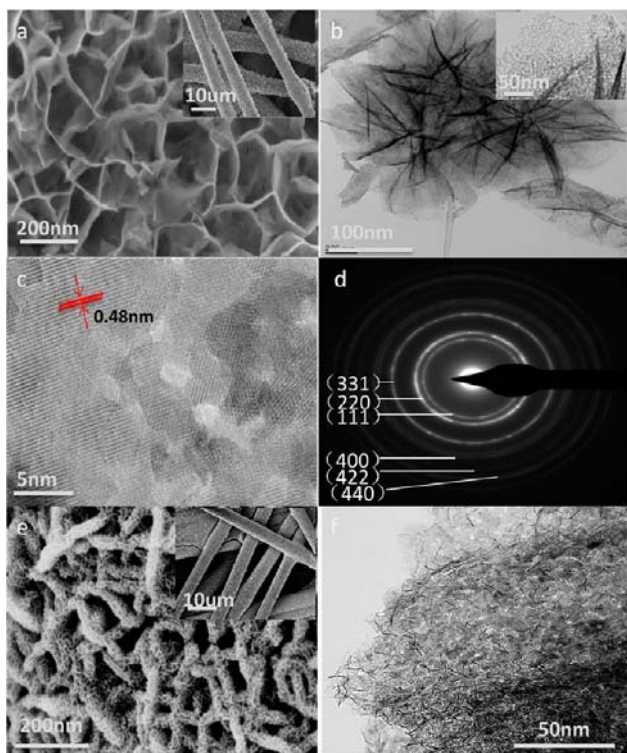


Figure 1. (a) SEM image of CFP after growth of NiCo_2O_4 nanosheets; (b, c) TEM image and HRTEM image of NiCo_2O_4 nanosheets. (d) Diffraction pattern of a NiCo_2O_4 nanosheets. (e) SEM image of a $\text{Ni}(\text{OH})_2$ coating on NiCo_2O_4 nanosheets grown on CFP. (f) TEM image of $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4$ hybrid composite grown on CFP.

the CFP with large surface area could offer favorable access to the electrolyte and enhance the ionic conductivity. The porous NiCo_2O_4 between CFP and $\text{Ni}(\text{OH})_2$ could increase the electronic conduction through the electrode and allows high utilization of active materials. All these features of this hybrid electrode offer the potential for high-performance supercapacitors. To confirm the advantage of NiCo_2O_4 for high performance of this electrode, we prepared a $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$ electrode (without adding the Ni source in the first step) for direct comparison under the same conditions (see Figures S2 and S3 in the Supporting Information).

Further, Raman spectroscopy was also used to characterize the phase composition of the $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4$ hybrid structure. As seen in Figure S5 in the Supporting Information, the peaks at 186, 480, 529, and 668 cm^{-1} correspond to F_{2g} , E_g , F_{2g} , and A_g models of the NiCo_2O_4 sheets, respectively²⁵ (see Figure S5 in the Supporting Information). After electrodeposition of a $\text{Ni}(\text{OH})_2$ coating, a new peak at 527 cm^{-1} was observed, corresponding to the stretching Ni–O (H) bond.^{11,24}

Then, we investigated the electrochemical performance of the hybrid composite $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$ and $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$ in the supercapacitors electrode application. All the measurement was carried out in a three-electrode cell system with 1 M KOH solution as electrolyte. The cyclic voltammetry (CV) performance of $\text{NiCo}_2\text{O}_4/\text{CFP}$ and $\text{Co}_3\text{O}_4/\text{CFP}$ before and after the deposition of $\text{Ni}(\text{OH})_2$ at a scan rate of 5 mV/s in the potential window of 0–0.6 V is shown in Figure 2a. Without coating $\text{Ni}(\text{OH})_2$, the $\text{Co}_3\text{O}_4/\text{CFP}$ and $\text{NiCo}_2\text{O}_4/\text{CFP}$ just show very weak redox peak, indicating poor electrochemical performance. After coating the $\text{Ni}(\text{OH})_2$ for 10 min, a significant

enhancement in the CV curve with a pair of redox peaks is observed, which can be attributed to the reversible Faradaic redox reactions of $\text{Ni}(\text{OH})_2$ materials. The redox potential at 0.4–0.5 V for $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$ and $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$ also matches the previous report used $\text{Ni}(\text{OH})_2$ as active materials for the supercapacitors application.²⁵ Analysis of the CV curves suggest that both $\text{Co}_3\text{O}_4/\text{CFP}$ and $\text{NiCo}_2\text{O}_4/\text{CFP}$ may serve mainly as the current collector, making little contribution to the capacitance of the electrodes.

The galvanostatic charge–discharge characteristic of hybrid composite within the potential range of 0–0.45 V at a current density of 5 mA/cm^2 is shown in Figure 2b. Obviously, the discharge curve can be divided into two sections, a sudden potential drop due to the internal resistance and a slow potential decay due to the Faradic redox reaction. This phenomenon suggests the pseudo-capacitance in our cell system (see Figure S6 in the Supporting Information). The areal capacitance (AC) and specific capacitance (SC) were calculated using eqs 1 and 2 (Supporting information). The AC of the $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$ and $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$ at a current density of 5 mA/cm^2 is 5.2 and 3.3 F/cm^2 , respectively, which is ~ 18 and ~ 12 times higher than the AC of $\text{NiCo}_2\text{O}_4/\text{CFP}$ and $\text{Co}_3\text{O}_4/\text{CFP}$ at the same current density. (Figure 2c) The highest SC of $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$ and $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$ base on the total mass (including the weight of CFP, metal oxide and hydroxyl oxide) is 464 and 291 F/g , respectively, with capacitance retention of 78 and 69% as the current density is increased from 2 to 50 mA/cm^2 . This performance is superior to that previously reported for the $\text{Ni}(\text{OH})_2/\text{CoO}$ walls on the nickel foam, which showed a capacitance retention of 57% when the current density was increased from 2 to 40 mA/cm^2 .²⁰ (Figure 2d) The remarkable performance and rate capability of $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$, compared to $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$, the higher conductivity of NiCo_2O_4 than Co_3O_4 , which improve the utilization of $\text{Ni}(\text{OH})_2$ coating during cycling. In fact, when the mass of CFP is excluded (i.e., only the mass of metal oxide and hydroxide is considered) in the calculation of capacitance per unit weight of active materials, the specific capacitance of hybrid composite $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4$ is ~ 3200 F/g at a current density of 2 mA/cm^2 (see Figure S7 in the Supporting Information).

The cycle life of these hybrid composite electrodes over 1 000 cycles was tested at a current density of 5 mA/cm^2 under galvanostatic charge/discharge cycling in the potential range from 0 to 0.45 V. As shown in Figure S8 in the Supporting Information, the areal capacitance of $\text{Ni}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{CFP}$ and $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$ dropped over 64% after 1 000 cycles, but impressive areal and specific capacitances as well as the rate capability suggest that the hybrid structure are suited for high-performance supercapacitors. Moreover, the morphology of $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$ was retained well after 1000 cycles, indicating a highly stable architecture of this hybrid composite. (Figure 3) To identify the cause of the performance loss during cycling, we performed thermogravimetric analysis (TGA) and BET surface area analysis of hybrid composite samples before and after the cycling measurements. The TGA data suggest that the mass of the active materials ($\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4$) is relatively stable during the cycling (the mass loading still remained at $\sim 16\%$). However, the specific surface area of the hybrid composite electrodes decreased more than 80% after 1000 cycles, as shown in Figure S10 in the Supporting Information. Thus, the decrease in specific surface area is the main cause of the poor cycling stability of the $\text{Ni}(\text{OH})_2/\text{NiCo}_2\text{O}_4/\text{CFP}$.

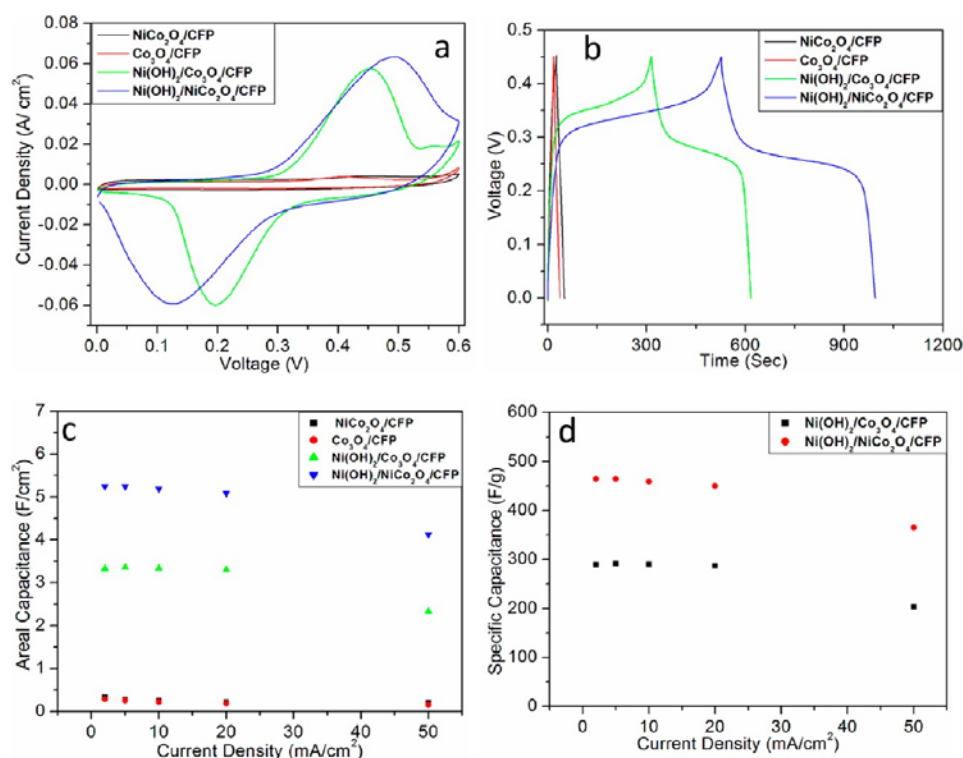


Figure 2. (a) Cyclic voltammograms of NiCo₂O₄/CFP, Co₃O₄/CFP, Ni(OH)₂/Co₃O₄/CFP, and Ni(OH)₂/NiCo₂O₄/CFP composite electrode in a 3-electrode cell with 1M KOH aqueous solution at scan rates of 5 mV/s. (b) Charge and discharge curves of hybrid composite electrodes at a current density of 5 mA/cm². (c) Areal capacitances of hybrid composite electrodes at different current densities. (d) Specific capacitance of hybrid composite electrodes at different current density (base on total mass of electrode).

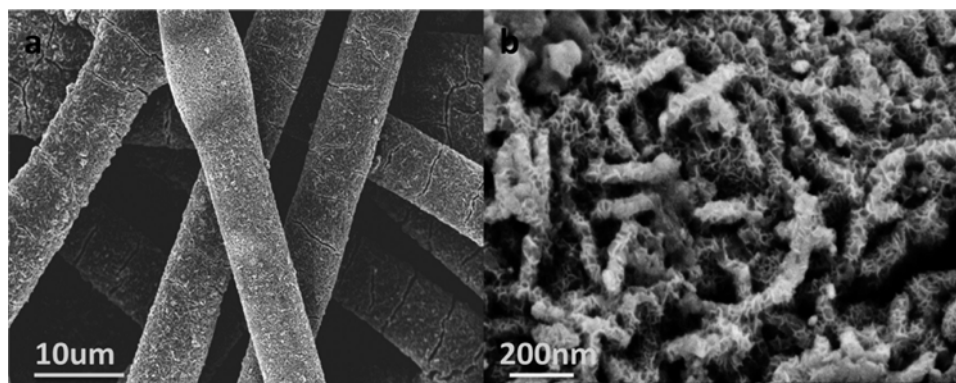


Figure 3. (a, b) Low- and high-magnification SEM image of Ni(OH)₂/NiCo₂O₄/CFP after 1000 cycles at current density of 5 mA/cm².

Careful analyses of the microstructures of the Ni(OH)₂/NiCo₂O₄/CFP electrodes suggest that their high specific capacitance and remarkable rate capability when used as electrochemical pseudocapacitors, are attributed to the following unique features. First, the CFP network with high conductivity allows efficient current collection or rapid electron transport to and from the electrochemically active materials. Second, the mesoporous, ultrathin NiCo₂O₄ sheets and Ni(OH)₂ plates provide sufficient open spaces and a shorter ion diffusion path for fast ionic transport, leading to higher utilization of active materials.

In summary, hybrid composites Ni(OH)₂/Co₃O₄ and Ni(OH)₂/NiCo₂O₄ directly grown on CFP were used as electrodes for supercapacitors. The electrochemical performances of the Ni(OH)₂/NiCo₂O₄/CFP are better than those of the Ni(OH)₂/

Co₃O₄/CFP electrode, demonstrating higher specific capacitance and rate capability. The capacitance retention is about 79% as the cycling current density was increased from 2 to 50 mA/cm².

ASSOCIATED CONTENT

Supporting Information

Synthesis detail of hybrid composite Ni(OH)₂/NiCo₂O₄ and Ni(OH)₂/Co₃O₄. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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