Transition metal oxide@hydroxide assemblies as electrode materials for asymmetric hybrid capacitors with excellent cycling stabilities

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In this work, three-dimensional cactus-like Co3O4@Ni(OH)2 electrode materials are grown directly on Ni foam via a two-step hydrothermal method. The as-prepared products possess a specific capacitance of 464.5 C g⁻¹ at 0.5 A g⁻¹ and 91.67% capacitance retention after 20 000 cycles. The as-assembled device using the as-synthesized samples as positive electrodes delivers an energy density of 112.5 W h kg⁻¹ at a power density of 1350 W h kg⁻¹. The superior electrochemical performance of the electrode materials can be attributed to their unique structure, the synergistic effect between Co3O4 and Ni(OH)2 materials and reversible reaction kinetics. It suggests that the products are potential alternatives in future energy storage devices.

1. Introduction

With the increasing depletion of fossil fuels and serious environmental pollution, to develop and design clean, renewable energy sources and emerging energy storage devices is a very imperative task. Among them, supercapacitors have attracted increasing attention due to their fast charging-discharging, high power density, long cycle life and environmental friendly characteristics. Carbon materials and conductive polymers with high specific surface area and low internal resistance have been widely investigated. For example, Fang and co-workers reported hierarchical porous carbon nanorods with a capacitance of 2384.3 F g⁻¹ at 1 A g⁻¹. Liu et al. prepared MoS2/Ni3S2@PPy samples showing a specific capacitance of 845 C g⁻¹ at 1 A g⁻¹. However, poor cycling stability hinders their further application. Therefore, it is urgent to develop novel electrode materials with the desired architectures and properties.

As electrode materials, transition metal oxides and hydroxides possess large theoretical capacity and accessible active sites for redox reaction. Therein Co3O4 materials possess a theoretical capacitance of 3500 F g⁻¹ and tailoring spatial structures. Many research groups have reported Co3O4 structures as electrode materials with various shapes and structures for capacitors. For instance, Zhang et al. in situ synthesized Co3O4 samples by a facile hydrothermal reaction with a capacitance of 621.8 F g⁻¹ at 1 A g⁻¹. Chen and co-worker reported Co3O4 nanorod arrays by chemical bath deposition showing a capacitance of 387.25 F g⁻¹ at 1 A g⁻¹. Gao et al. prepared Co3O4 nanowires using a template-free process and obtained a capacitance of 746 F g⁻¹ at 1 A g⁻¹. Nevertheless, the practical capacity is far lower than their theoretical one, which limits their future applications in energy storage fields. Two dimensional layered Ni(OH)2 nanostructures enable fast diffusion of electrons, which make active sites for redox reaction easily accessible. For example, Yang’s group reported Ni(OH)2 electrode exhibiting a specific capacitance of 2110 F g⁻¹ at 1 A g⁻¹. Xiong et al. synthesized Ni(OH)2 nanosheets with a capacitance of 2384.3 F g⁻¹ at 1 A g⁻¹. Dai et al. prepared Ni(OH)2 nanocrystals grown on graphene sheets showing a capacitance of 1335 F g⁻¹ at 1 A g⁻¹. Herein, we design a kind of cactus-like Co3O4@Ni(OH)2 structure on Ni foam through a facile two-step hydrothermal approach. The as-prepared products show a specific capacitance of 464.5 C g⁻¹ at 0.5 A g⁻¹ and 91.67% of capacitance retention after 20 000 cycles. A capacitor is assembled using Co3O4@Ni(OH)2 as positive electrode and active carbon as negative electrode, respectively. It delivers an energy density of 112.5 W h kg⁻¹ at power density of 1350 W h kg⁻¹. The excellent performance could be attributed to fast ion transport channel, which constructed by direct contact between two materials and synergistic effect.

2. Experimental

All the chemicals in this work are of analytical grade and directly used without further purification. Ni foam was treated, which is similar to our previous report. In a typical procedure, 3 mmol Co(NO3)2·6H2O (0.8731 g), 4 mmol NH4F (0.1482 g) and 10 mmol CO(NH2)2 (0.6006 g) were dissolved in 50 mL deionized water and stirred to form a homogeneous solution. Then...
samples were cleaned and then dried at 60 °C for 2 h. The average mass loading is 2.1 mg cm⁻².

Electrolyte. Specific discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were conducted in 3 M KOH aqueous solution. The samples were used as supercapacitor. Quasi-solid-state polyvinyl alcohol (PVA)-KOH electrolyte was made by mixing 2 g PVA and 2 g KOH in 20 mL deionized water. The mass loading of active carbon was calculated based on charge balance theory (Eq. (7)).

Activated carbon, super p and polyvinylidene difluoride (PVDF) with a mass ratio of 7:2:1 were mixed on Ni foam as negative electrode for supercapacitor. Quasi-solid-state polyvinyl alcohol (PVA)-KOH electrolyte was made by mixing 2 g PVA and 2 g KOH in 20 mL deionized water. The mass loading of active carbon was calculated based on charge balance theory (Eq. (7)). The phase purity and crystal structure of products are firstly characterized by XRD, as shown in Fig. 1a. All diffraction peaks (black line) of samples located at 19.0° (111), 31.2° (220), 36.8° (311), 38.5° (222), 55.6° (422), 59.3° (511) and 65.2° (440) can be indexed to Co₃O₄ (JCPDS No.42-1467). The diffraction peaks (red line) at 19.2°, 33.1°, 39.1° and 62.7° correspond to Ni(OH)₂ (001), (100), (002), (110), (111) crystal planes, which can be assigned to Ni(OH)₂ (JCPDS No.14-0117). From the diffraction peaks (blue line), Co₃O₄@Ni(OH)₂ products are successfully prepared.

XPS is used to further study elemental composition and chemical states of products. The survey spectra (Fig. 1b) show the presence of Co, Ni and O elements. C is from the base. The de-convolution of Ni 2p XPS spectra in Fig. 1c presents two characteristic peaks of Ni 2p₃/2 and Ni 2p₁/2 at 855.5 and 873.1 eV and two satellite peaks at 862 and 879 eV, respectively. Fig. 1d indicates that Co 2p spectra consist of Co²⁺ and Co³⁺. It could be de-convoluted into two sharp peaks and two satellite peaks. The peaks at 779.3 and 794.5 eV are related to Co³⁺ and those at 781 and 796.2 eV might be ascribed to Co²⁺. The peaks of O 1s spectra (Fig. 1e) at 529.7, 531.2 and 532.5 eV are associated with metal–oxygen bond, hydroxyl (OH⁻) and surface absorbed water, respectively. Elemental distributions of products are also investigated by element mappings, demonstrating that elements are uniformly distributed on the Ni foam, as shown in Fig. 1f.

Fig. 2a is SEM images of as-prepared Co₃O₄ products. It shows that they consist of many nanowires. Further observation (Fig. 2d) finds that the average diameter of the nanowires is 70 nm. Fig. 2b shows SEM images of Ni(OH)₂ sample, revealing that dense sheet-like structures appear. Local images can be seen in Fig. 2e. From SEM images shown in Fig. 2c and f, it is found that hybrid materials consist of many nanowires and nanosheets that interconnect with each other to form unique three-dimensional cactus-like structures.

Electrochemical performances of as-synthesized products are studied in 3 M KOH aqueous solution in a three-electrode system. Fig. 3a-c show CV curves of three electrodes at scan rate from 5 to 50 mV s⁻¹. CV curves of composite electrode present a pair of redox peaks, revealing that capacitive behavior of electrode materials. The redox peaks correspond to faradaic redox reactions during charging-discharging process as follows:

\[
P = E \times 3600/\Delta t
g
\]

where \(\Delta V(V)\) is voltage window of device, \(\Delta t(s)\) is discharge time.

### 3. Results and discussion

The morphology and crystal structure of as-prepared products were investigated on a workstation (Shanghai Chenhua, CHI660E) in a three-electrode system. The samples were used as negative electrode for supercapacitor. Quasi-solid-state polyvinyl alcohol (PVA)-KOH electrolyte was made by mixing 2 g PVA and 2 g KOH in 20 mL deionized water. The mass loading of active carbon was calculated based on charge balance theory (Eq. (7)).

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\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3\text{CoOOH} + \text{e}^- \quad (6)
\]

\[
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (7)
\]

\[
\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \quad (8)
\]
The shapes of CV curves maintains well, indicating excellent reversibility of redox reaction. The corresponding GCD curves of samples are shown in Fig. 3d–f. According to GCD curves of hybrid electrodes at various current densities, specific capacitances are 464.5, 407, 322, 240, and 180 C g\(^{-1}\) at 0.5, 1, 2, 4 and 6 A g\(^{-1}\), respectively.

Fig. 4a shows CV curves of as-synthesized products and pure Ni foam at 20 mV s\(^{-1}\). Obviously, the effect of pure Ni foam on capacities of the samples can be neglected due to its insignificant contribution. It is accordance with previous reports.\(^4\) The integrated area of CV curve of Co\(_3\)O\(_4@\)Ni(OH)\(_2\) samples is relatively larger, suggesting that composite electrode possesses a high capacitance. Fig. 4b shows GCD curves of three electrode
materials at the same current density. The discharge time of hybrid electrode is longer than two other samples.

To further investigate the conductivity of as-synthesized products, EIS are conducted within frequency range from 0.01 to $10^5$ Hz. Fig. 4c demonstrates Nyquist plots of all samples, which include a semicircle at high frequency region and a straight line at low frequency one. The former represents equivalent series resistance ($R_{SE}$), the latter corresponds to Warburg resistance. $R_{SE}$ of $\text{Co}_3\text{O}_4@\text{Ni(OH)}_2$, $\text{Co}_3\text{O}_4$, $\text{Ni(OH)}_2$ are 0.74, 0.88, 1.45 ohm cm$^{-2}$, respectively, suggesting that hybrid electrode possesses a low internal resistance.
To understand surface and diffusion behavior of electrodes, the normalization formulas for CV kinetics analysis are listed as follows:

\[ i = av^b \]

(9)

\[ \frac{i}{v^{1/2}} = av^{1/2} + b \]

(10)

where \( a \) and \( b \) are constants, \( i \) and \( v \) represent current and scan rate, respectively. As shown in Fig. 4d, diffusion controlled contribution is dominant, revealing that battery-type behavior of electrode materials. Cycling stabilities (Fig. 4e) of as-synthesized samples are investigated at 6 A g\(^{-1}\). It can be seen that the capacitance retention ratio of hybrid electrode can reach 91.67% after 20 000 cycles, which is much higher than other two ones. The excellent cycling stability might benefit from synergistic effect between two electrodes. The activation of electrode materials results in the increases of specific capacitance in the initial cycles. With the adding of cycle times, electrode materials are gradually infiltrated by electrolyte, which results in an increase in capacitance.

To estimate its practical application, a hybrid capacitor is assembled using as-prepared products and active carbon as positive and negative electrodes, respectively. CV curves of two electrodes show stable voltage windows between 0 and 0.6 V and between −1 and 0 V, respectively (Fig. 5a). The curves at 50 mV s\(^{-1}\) indicate that the device can work at 1.6 V, as shown in Fig. 5b. CV curves of device at scan rates from 5 to 50 mV s\(^{-1}\) (Fig. 5c) exhibits that it possesses ideal capacitive performance. According to GCD curves at various current densities (Fig. 5d), the device delivers a capacitance of 150 C g\(^{-1}\) at 0.5 A g\(^{-1}\). It keeps 87% of initial capacitance after 6000 cycles in Fig. 5e.

Energy density and power density of device are two significant parameters in actual applications. Fig. 5f shows Ragone plots of some devices. The device presents an energy density of 112.5 W h kg\(^{-1}\) at power density of 1350 W kg\(^{-1}\), which are better than some previous reports.\(^{32,43−45}\) According to Table 1, the hybrid electrode materials reported here possess high specific capacitance and excellent cycling stability.\(^{23,46−49}\)

![Fig. 5](image-url)

(a) CV curves of Co\(_3\)O\(_4\)@Ni(OH)\(_2\) and AC electrode at 20 mV s\(^{-1}\) (b and c) CV curves of device (d) GCD curves (e) cycling performance (f) Ragone plot.

**Table 1** Electrochemical performance comparison of various electrode materials

| Materials                                   | Specific capacitance (1 A g\(^{-1}\)) | Electrolyte  | Retention rate                  | Ref.  |
|---------------------------------------------|--------------------------------------|--------------|---------------------------------|-------|
| Co\(_3\)O\(_4\) mesoporous nanoneedle       | 668 F g\(^{-1}\) (367.4 C g\(^{-1}\)) | 2 M KOH      | 104% (10 000 cycles)            | 23    |
| 2D-Co(OH)\(_2\)/Co\(_3\)O\(_4\) flakes     | 583 F g\(^{-1}\) (291.5 C g\(^{-1}\)) | 2 M KOH      | 87.6% (1000 cycles)             | 46    |
| Sandwich-like Co\(_3\)O\(_4\)/CNTs         | 562 F g\(^{-1}\) (252.9 C g\(^{-1}\)) | 3 M KOH      | 96% (5000 cycles)               | 47    |
| 2D MoSe\(_2\)−Ni(OH)\(_2\) nanohybrid      | 933 F g\(^{-1}\) (419 C g\(^{-1}\))  | 6 M KOH      | 91.6% (5000 cycles)             | 48    |
| Co\(_3\)O\(_4\) nanosheets                  | 581 F g\(^{-1}\) (261.4 C g\(^{-1}\)) | 2 M KOH      | 91% (5000 cycles)               | 49    |
| Co\(_3\)O\(_4\)@Ni(OH)\(_2\) cactus        | 407 C g\(^{-1}\)                    | 3 M KOH      | 91.67% (20 000 cycles)          | This work |
4. Conclusion

In summary, we have fabricated a kind of cactus-like 3D Co$_3$O$_4$@Ni(OH)$_2$ structure on Ni foam via two-step hydrothermal process. Benefiting from the unique architecture, the as-obtained products possess superior electrochemical performances due to the synergistic effects between two single materials. Moreover, the device presents high energy density and excellent cycling stability. It demonstrates that the hybrid architectures can be used as alternative electrode materials in high-performance energy storage devices.

Conflicts of interest

There are no conflicts to declare.

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