ACS APPLIED MATERIALS & INTERFACES

Alternating Voltage Introduced NiCo Double Hydroxide Layered Nanoflakes for an Asymmetric Supercapacitor

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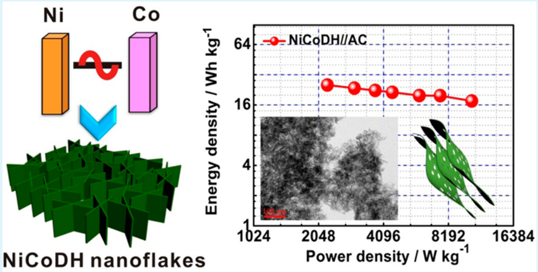
Supporting Information

ABSTRACT: An electrochemical alternating voltage approach of producing NiCo double hydroxide (NiCoDH) layered ultrathin nanoflakes with large specific surface area (355.8 $m^2\ g^{-1}$), remarkable specific capacitance and rate capability is presented. The obtained NiCoDH as anode for asymmetric supercapacitors shows excellent energy density of 17.5 Wh kg^{-1} at high power density of 10.5 kW kg^{-1} and cycling stability (91.2% after 10 000 cycles).



KEYWORDS: *alternating voltage, NiCo double hydroxide, electrochemical, nanoflakes, asymmetric supercapacitors*

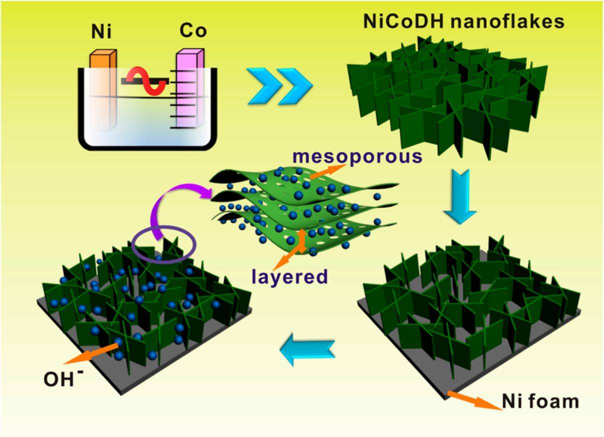
Supercapacitors, also known as electrochemical storage devices, have attracted extensive attentions because of characteristics such as high power density, long cycling stability, and improved safety in the modern electronics.[1,2] An critical factor determining electrochemical performances of supercapacitors is the properties of active electrode material.[3] At present, various binary oxides/hydroxides are quite intriguing because they exhibit markedly higher capacitance than that of the monometallic oxides/hydroxides.[4−6]

Among these, more research attention has been attracted by Ni_xCo_{1-x} double hydroxide material than any other binary oxides/hydroxides because of its high specific capacitance and tunable microstructure.[7−9] For instance, $Co_{0.5}Ni_{0.5}$ hydroxide displayed a high specific capacitance of 1500 F g^{-1}.[10] However, the Ni_xCo_{1-x} double hydroxide electrode still suffers from either low rate capability, or low energy density (at high power density). Note that layered double hydroxides as the active electrochemical material are of particular concentration.[1,10,11] To achieve this special construction, various methods have been reported to fabricate metallic double hydroxides, for instances: template technique,[6] potentiostatic deposition,[12] microwave reflux,[13] to name just a few. However, most of them are time-consuming and complex. Recently, alternating voltage method as a simple and green approach has been developed to prepare metal oxide nanocrystals with one-step.[14,15]

In the present work, an electrochemical alternating voltage approach was first undertaken to synthesize NiCoDH layered ultrathin nanoflakes. The as-obtained NiCoDH demonstrate excellent electrochemical performances for supercapacitor. Moreover, asymmetric supercapacitor was assembled with NiCoDH as the positive electrode, exhibiting an energy density of 17.5 Wh kg^{-1} at high power density of 10.5 kW kg^{-1}.

A new green alternating voltage strategy was designed and used for the preparation of NiCoDH. The detailed procedure is described in the Supporting Information. The electrochemical mechanism of NiCoDH nanoflakes by alternate voltage utilizing Ni and Co electrodes is illustrated in Scheme 1. First, pure Ni and Co electrodes can be oxidized anodically to form high valence metal oxides films. While the voltage was

Scheme 1. Schematic Illustration for the Preparation of NiCoDH Layered Nanoflake Electrode



Received: June 25, 2015
Accepted: October 5, 2015
Published: October 5, 2015

DOI: 10.1021/acsami.5b05660
ACS Appl. Mater. Interfaces 2015, 7, 22741−22744

switched to cathodic polarization, the high valence metal oxides were reduced to low valence hydroxides in NaCl solution, accompanying substantive hydrogen evolution. Finally, the metal hydroxides were gradually swept away from the surface of electrodes and formed to NiCoDH nanoflakes with mesopore structure through layer-by-layer self-assembly under alternating electric field. It is stressing that the ultrathin flakes network structure can provide rich electroactive sites and efficient pathways for charge (OH^-) transport. Furthermore, the layered structure and suitable mesopore size distribution can contribute better penetration of electrolyte into the electrode materials and can also shorten path length for rapid transport of ions and electrons even at high rates.[1,16]

The morphology and structure of the NiCoDH nanoflakes were studied by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM), as shown in Figure 1 and Figure S1. It can be seen that the NiCoDH sample displays ultrathin nanoflakes which exhibit wrinkle-like appearances with numerous mesoporous. Figure S2 displays the thickness of NiCoDH nanoflakes is about 5 nm. Moreover, the HRTEM image reveals lattice fringes of 0.258 nm correspond to the (012) crystal plane and the nanoflakes layered structure is observed,[17,18] which is very important for faster redox reactions.[19,20]

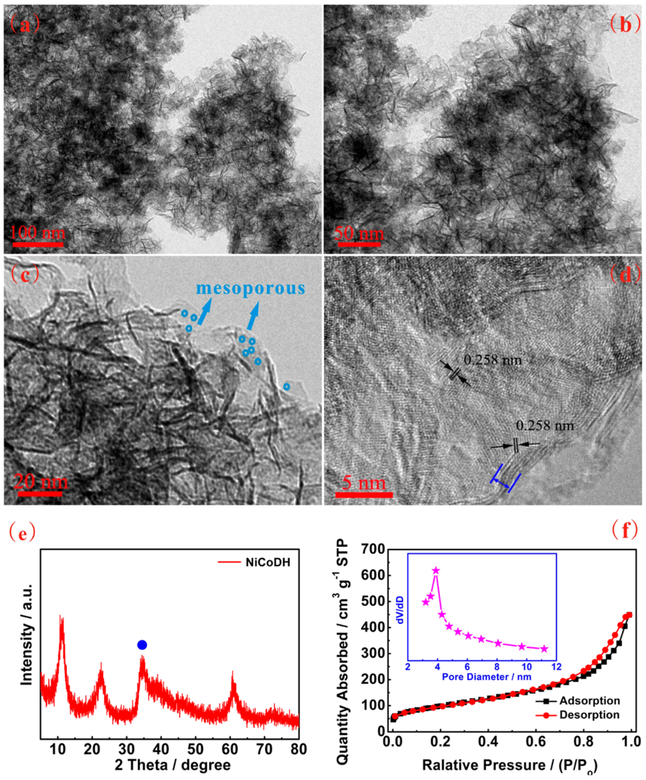


Figure 1. (a−c) TEM and (d) HRTEM images of NiCoDH. (e) XRD pattern of NiCoDH. (f) Nitrogen adsorption and desorption isotherm of the NiCoDH sample and the inset shows the corresponding BJH pore size distribution curve.

The phase of NiCoDH was determined through X-ray diffraction (XRD) tests, which is presented in Figure 1e. Where, well-defined diffraction peaks observed at 2θ values of 11.2, 22.8, 34.4, and 60.65° correspond to hydrotalcite-like NiCoDH phase. The *d*-spacing between the basal planes of the NiCoDH was determined to be 7.67 Å which is between the 7.56 Å of pure α-$Ni(OH)_2$ and the 7.75 Å of pure α-$Co(OH)_2$.[5,21] Additionally, the characteristic asymmetric peak at 2θ of 34° is due to "two-dimensional" reflection of the turbostratically stacked unit cell,[15] suggesting the NiCoDH nanoflakes are well-mixed layered structure which is agreeing well with the HRTEM results. Furthermore, the energy dispersive X-ray (EDX) mapping of NiCoDH (Figure S3) shows that both Ni and Co distribute uniformly and continuously in the NiCoDH sample and no obvious phase segregation is observed. And the result of inductively coupled plasma (ICP) emission spectrometry analysis illustrate the atom ratio of Ni and Co is almost 1:1. Additionally, the X-ray Photoelectron Spectroscopy (XPS, Figure S4) further confirms the formation of NiCoDH through the alternating voltage method with the presence of Ni^{2+} and Co^{2+} components.[2,18,22] Figure 1f displays specific surface area (SSA) of the NiCoDH is calculated to be 355.8 $m^2\ g^{-1}$ from the nitrogen adsorption−desorption isotherm. Moreover, the mesoporous structure was further confirmed by the Barrett−Joyner−Halenda (BJH) pore size distribution data (the inset of Figure 1f), with the pore distribution mainly centered about 3.8 nm. This kind of NiCoDH nanoflakes with high specific surface area and suitable mesopore distribution is believed to be extremely beneficial for supercapacitors.

Electrochemical performances of the NiCoDH nanoflakes were investigated in a typical three-electrode configuration. Figure 2a demonstrates a set of cyclic voltammogram (CV) curves of NiCoDH electrode in the potential window of 0−0.6 V (vs Hg/HgO). The obvious redox peaks are unequivocally defined, which relate to redox reactions (eqs 1 and 2).[5]

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O \qquad (1)$$

$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O \qquad (2)$$

Compared with previous reports of separated redox peaks from $Co(OH)_2$, there is only one pair of redox peaks, suggesting nickel and cobalt hydroxides are well-mixed in NiCoDH which is consistent with the XRD and EDX analysis. Additionally, the inset in Figure 2a indicates the specific capacitance of substrate could be negligible. Besides, both reduction and oxidation peak currents were increased with only slightly change with the increased scan rate from 5 to 100 mV s^{-1}, which demonstrates good reversibility of fast charge−discharge response of the NiCoDH electrode.[2,23]

Figure 2b, c show the specific capacitance values of the NiCoDH electrode calculated from the charge−discharge curves are 1372, 1331, 1253, 1166, 1092, 1032, and 930 F g^{-1} at current densities of 1, 2, 5, 10, 15, 20, and 30 A g^{-1}, respectively. The capacity retention rate (compared with 1 A g^{-1}) of the NiCoDH is up to 79.2 and 67.8% when the current density increases to 15 and 30 A g^{-1}, respectively. In Figure 2d, the NiCoDH electrode exhibits a quiet small semicircle with the value of about 0.35 Ω in the high-frequency region, suggesting a particularly low charge transfer resistance. Also, the NiCoDH electrode displays high slope in the low-frequency region, which indicates the more facile electrolyte ions diffusion to the active material.[15] Hence, the NiCoDH electrode can remain outstanding rate capability. The cycling stability of NiCoDH nanoflakes was further measured at 2 A g^{-1} (Figure S5). It delivers a good cycling performance with 94.3% after 2000 cycles (Table S1). All these enhanced electrochemical behaviors of NiCoDH electrode can be attributed to the special structure of the as-prepared NiCoDH with high specific surface area, layer structure, and suitable mesopore size distribution.

DOI: 10.1021/acsami.5b05660
ACS Appl. Mater. Interfaces 2015, 7, 22741−22744

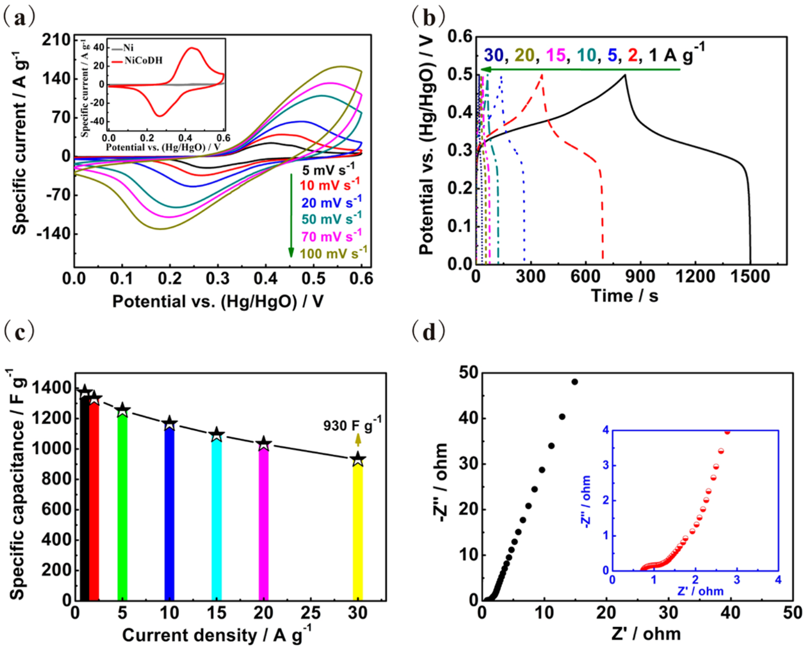


Figure 2. (a) CV curves of the NiCoDH electrode at various scan rates in a three-electrode system, and the inset showing the CV curves of bare Ni and NiCoDH at 10 mV s^{-1}. Galvanostatic charge−discharge curves (b) and rate capability (c) of the NiCoDH electrode at various current densities. (d) Nyquist impedance plot of the NiCoDH electrode and the inset shows a magnification of the impedance spectra.

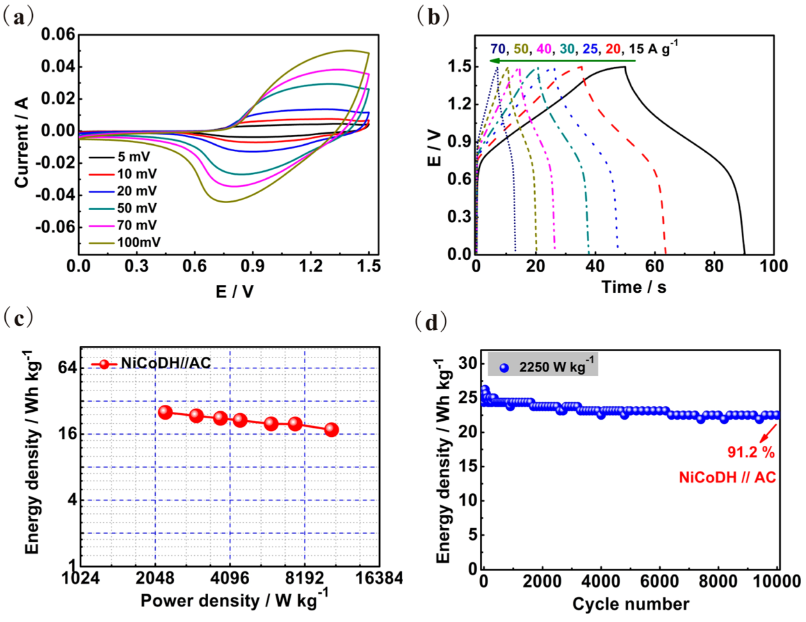


Figure 3. (a) CV curves and (b) galvanostatic charge and discharge curves of the NiCoDH//AC asymmetric supercapacitor. (c) Ragone plots of the asymmetric supercapacitors. (d) Cycle life of NiCoDH//AC at the power density of 2250 W kg^{-1}.

An asymmetric supercapacitor was fabricated by utilizing NiCoDH and active carbon (AC). Figure 3a displays the CV curves of NiCoDH//AC asymmetric supercapacitor at various scan rates. As expected, the relatively stable potential window of NiCoDH//AC can be extended to 1.5 V. Moreover, with the increase of scan rate from 5 to 100 mV s^{-1}, the shapes of CV curves have not been obviously changed, implying the NiCoDH//AC exhibits good capacitive behavior. The charge−discharge curves of NiCoDH//AC with cell voltage as high as 1.5 V were shown in Figure 3b at various current densities from 15 to 70 A g^{-1}. Figure 3c shows the Ragone plots of the corresponding energy and power densities for the NiCoDH//AC, which delivers an energy density of 25.3 Wh kg^{-1} at a power density of 2250 W kg^{-1} (15 A g^{-1}). Even at an ultrahigh power density of 10.5 kW kg^{-1} (70 A g^{-1}), the energy density of NiCoDH//AC still retains 17.5 Wh kg^{-1}, which is comparable to the state-of-the-art NiCoDH materials.[2,5] Additionally, the NiCoDH//AC cell maintains 91.2% after 10000 cycles at 2250 W kg^{-1} (Figure 3d), revealing its excellent electrochemical stability. All these results render the NiCoDH//AC would become a promising energy storage device with both high energy and power densities.

In summary, an electrochemical alternating voltage approach has been first developed to prepare NiCoDH with one-step.

DOI: 10.1021/acsami.5b05660
ACS Appl. Mater. Interfaces 2015, 7, 22741−22744

The ultrathin NiCoDH layered nanoflakes with high specific surface area (355.8 m^2 g^{-1}) and suitable mesopore size distribution presents high specific capacitance (1166 F g^{-1} at 10 A g^{-1}), remarkable rate capability (67.8% capacity retention from 1 to 30 A g^{-1}), and good cycling stability. In addition, fabricating the asymmetric supercapacitor with utilizing NiCoDH nanoflakes exhibits high energy density of 17.5 Wh kg^{-1} at an outstanding high power density of 10.5 kW kg^{-1} and excellent cycling stability of 91.2% retention over 10 000 cycles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05660.

Experimental details, Figures S1−S5, and Table S1 (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by National Natural Science Foundation of China (21473258), Distinguished Young Scientists of Hunan Province (13JJ1004), the Hunan Provincial Innovation Foundation for Postgraduate (CX2015B039), Grants from the Project of Innovation-driven Plan in Central South University, and the State Key Laboratory of Powder Metallurgy, Central South University, Changsha, China.

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