Supplementary Information

NiCo Layered Double Hydroxide Nanocages for High

Performance Asymmetric Supercapacitors

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1.General Information

1.1.Materials

Polytetrafluoroethylene (PTFE), polyvinylpyrrolidone (PVP, K30), L-ascorbic acid, activated carbon (AC), graphitized carbon black, and $NiCl_2 \cdot 6H_2O$ were manufactured by Shanghai Macklin Biochemical Co., Ltd. $CoCl_2 \cdot 6H_2O$, $Na_2S_2O_3$ and absolute ethanol were purchased from Xilong Chemical Co., Ltd. $CuCl_2 \cdot 2H_2O$ was provided by Aladdin Chemical Co., Ltd. Nickel foam (denoted NF, the thickness and purity of NF were 1 mm and 99.9%, respectively) was purchased from Shenzhen Kejing Co. Ltd. No reagents were purified further. Deionized (DI) water was applied in all tests.

1.2.Material characterization

The structure and morphologies of the samples were studied by XRD (Cu Kα, λ=0.154 nm, Bruker D8 Advance), SEM (FEI Nova Nano SEM450), and TEM (TEM, Talos F200X). The surface chemical bonding states were analyzed by XPS (Thermo ESCALAB 250XI). The specific surface area and porous structure of the samples were studied via the BET method (BELSORP Max). The nickel and cobalt molar ratio of the samples were studied by ICP-MS(ICP-Ms:Aglient 7850). In situ investigations were conducted in an electrochemical three-electrode cell. The NiCo-LDH-1 electrode, silver/silver chloride and Pt plate electrode were applied as the working, reference and counter electrodes, respectively, in an electrochemical cell with 1 mol/L KOH. In situ XRD characterizations of NiCo-LDH-1 were tested at CV (0~0.45 V vs. Ag/AgCl; scanning rate: 0.6 mV·s-1). The change in the crystal structure in the 2θ region (5° - 80°) during the charge–discharge process was investigated.

2.Experimental section

2.1.Preparation of Cu_2O nanocubes

In brief, $CuCl_2 \cdot 2H_2O$ (0.17 g) was dissolved into 100 mL DI water under ambient conditions to produce a transparent light blue solution. After heating to 55°C, 2 mol·L^{-1} NaOH (10 mL) was slowly added to the light blue solution and stirred for 30 min. Then, 0.6 mol·L^{-1} L-ascorbic acid (10 mL) was added to the solution. After stirring for 3 h, a red precipitate was obtained. Subsequently, solid products (Cu_2O nanocubes) were obtained by centrifugation, alternately washed with DI water and absolute alcohol, and dried at 60°C.

2.2.Preparation of hollow NiCo-LDH nanocages

Based on the principle of Pearson hard and soft acid-base (HSAB), hollow cubic structures were prepared.[22] In a typical process, 120 mg Cu_2O powder was dispersed in 240 mL mixed solvent (1:1) containing water and ethanol. After 30 min of ultrasound, 3.6 g polyvinylpyrrolidone (PVP, K30) was added. After stirring for 30 min, $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ with molar ratios of 1:2, 1:1, and 2:1 were added to the solution. Then, 100 mL of $Na_2S_2O_3$ solution (1 $mol \cdot L^{-1}$) was added dropwise into the suspension at a 30 rpm/min rate through a peristaltic pump and stirred for 3 h until the red color of the suspension turned green. Subsequently, the powders were assembled by centrifugation, washed with DI water and absolute alcohol, and dried at 60°C for 12 h. The obtained solids were denoted NiCo-LDH-0.5, NiCo-LDH-1 and NiCo-LDH-2 according to the feeding molar ratios of Ni: Co.

2.3.Synthesis of $Ni(OH)_2$ and $Co(OH)_2$ nanocages

Similarly, using the protocol described in section of preparation of hollow NiCo-LDH nanocages, $Ni(OH)_2$ nanocages were prepared without the addition of $CoCl_2 \cdot 6H_2O$ and $Co(OH)_2$ nanocages were prepared without the addition of $NiCl_2 \cdot 6H_2O$.

2.4.Preparation of common NiCo-LDH

The common NiCo-LDH was prepared without the addition of a Cu_2O nanocube template. $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ with a molar ratio of 1:1 were dissolved in DI water (140 mL). Then, 1 $mol \cdot L^{-1}$ NaOH solution (100 mL) was added dropwise into the mixture via a peristaltic pump. The reaction was then stirred for 3 h. After centrifugation and washing with DI water and absolute alcohol, the collected products were dried at 60°C for 12 h. The resulting material was named NiCo-LDH-C.

2.5.Electrochemical characterization

The as-prepared NiCo layered double hydroxide was placed into a polyethylene plastic tube. Then, a mixture of 5 mg/mL carbon black, polytetrafluoroethylene (PTFE) and absolute ethanol solution (the mass ratio was 8:1:1) was mixed to obtain a suspension that was uniformly dispersed onto the surface of a nickel foam (NF) (the loading area and amount were 1×1 cm^2 and 2 mg, respectively) and dried at 60°C for 12 h and finally pressed into thin slices under a pressure of 10 MPa to obtain NiCo layered double hydroxide electrodes. Similarly, activated carbon electrodes were prepared by

activated carbon and polytetrafluoroethylene (PTFE) (the mass ratio was 8:2).

The two-electrode testing system (NiCo-LDH-1 and activated carbon electrodes were applied as positive and negative electrodes, respectively) was tested in 1 mol·L⁻¹ KOH. Testing GCD (galvanostatic charge-discharge), CV (cyclic voltammetry), EIS (electrochemical impedance spectroscopy), and so on, were conducted by a CHI 660E electrochemical workstation. The frequency range of EIS was 0.01~100000 Hz, and the electrolytes were Fe^{2+}/Fe^{3+} (0.25 mmol·L⁻¹, 0.25 mmol·L⁻¹) and Na_2SO_4 (0.5 mol·L⁻¹).

The mass of activated carbon to be loaded on the cathode can be calculated from the mass of NiCo layered double hydroxide loaded on the anode based on the following formula:[1]

$$\frac{m^+}{m^-} = \frac{C^- * \Delta v^-}{C^+ * \Delta v^+}$$

(1)

where m⁺/m⁻(g), C⁺/C⁻(F·g⁻¹), and ΔV⁺/ΔV⁻ (V) are the mass, capacitance values and voltage windows of the positive/negative materials, respectively.

The mass ratio capacitance (C_g, F·g⁻¹), energy density (E, Wh·kg⁻¹) and power density (P, W·kg⁻¹) can be expressed by the following formulas:[2]

$$C_g = \frac{I * \Delta t}{m * \Delta V}$$

(2)

$$E = \int \frac{I * \Delta V}{3.6m} dt$$

(3)

$$P = \frac{E}{\Delta t}$$

(4)

where t(s) is the discharging time. I(A) is the current during the charging and discharging process. m(g) is the weight of the active material. ΔV(V) is the potential window of the electrode.

Table S1 Weight ratios and atomic ratios of NiCo-LDH-1 Hollow Nanocages measured by EDX.

Element	Atomatic (%)	Weight (%)
Ni	20.87	36.52
Co	20.12	35.34
O	59.01	28.14

Table S2 Comparison of NiCo-LDH-1//AC with similar supercapacitor devices.

Supercapacitor device	Energy density (Wh·kg^{-1})	Power density (W·kg^{-1})	Voltage (V)	Ref.
HKUST-1@CoNi-LDH//AC	39.8	799.9	1.6	[3]
Ni2P/NiGa$_2$O$_4$/NiGa-LDH//Co$_3$O$_4$-C	72	800	1.6	[4]
Co-NiMn-LDH@V$_2$C//V$_2$C	30	700	1.4	[5]
NiMn-LDH@CuO//AC	10.8	100	1	[6]
CoAlNi-LDH-NR//AC	50.3	800	1.6	[7]
CoSx/Ni-Co LDH//AC	35.8	800	1.6	[8]
NiAl-LDH-OA-2//AC	40.26	943	1.6	[9]
NiCoP@NiCo-LDH//AC	57	850	1.7	[10]
CCCH@NiCo-LDH@Au-CuO/Cu//VN	34.97	1053	1.6	[11]
NiCo$_2$Al-LDH//CC@ZPC	44	462	1.5	[12]
NiFe-LDH/NiOOH//MoS$_2$/rGO	48.1	432.9	1.7	[13]
NiAl-LDH/rGO//AC	15.42	230	1.6	[14]
NiCo-LDH-1//AC	**59.0**	**935.7**	**1.6**	**This work**

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