Supplementary Information

Biomass Carbon Enabled Charge Transport Network Optimization in Layered Double Hydroxides for High-rate Energy Storage

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1. Supplementary Experimental Section

1.1 Chemicals:

The fresh wheat straw utilized in the experiments was purchased from Henan Province in China. Nickel nitrate hexahydrate (Ni(NO₃)₂· $6H_2O$, AR), cobaltous nitrate hexahydrate (Co(NO₃)₂· $6H_2O$, AR), calcium chloride (CaCl₂, AR), melamine, and potassium hydroxide (KOH, AR) were acquired from Macklin. Polytetrafluoroethylene (PTFE, 60 wt.% in H₂O) was obtained from Aladdin. Hexamethylene tetramine (HMTA, AR) and hydrochloric acid (HCl, AR) were sourced from Sinopharm Chemical Reagent Co., Ltd. All chemicals were utilized without additional purification.

1.2 Characterization of materials:

The surface morphology and structure of samples were observed using the field emission scanning electron microscopy (SEM, NERCN-TC-006) and transmission electron microscopy (TEM, TALOS F200X). Nitrogen sorption isotherms were measured with a Micromeritics ASAP 2020 adsorption analyzer. The XRD patterns of all samples were recorded using powder X-ray diffraction (Rigaku Ultima IV Powder Diffractometer). Raman spectra were recorded on a Renishaw inVia reflex spectrometer using laser excitation of 532 nm. X-ray photoelectron spectrometer (XPS) measurements were performed on a Thermo Scientific ESCALAB QXi X.

The contact angles measurement was performed on Automatic optical contact angle analyzer (KRUSS DSA100). The thermogravimetric results were tested by Simultaneous Thermal Analyzer (STA, NETZSCH-449 F3 Jupiter).

1.3 Electrochemical measurements and calculation:

The electrochemical performances were measured using an electrochemical workstation (Biologic VMP3) for both electrodes and devices. The active material was mixed with carbon black and PTFE in a mass ratio of 7:2:1 to prepare the electrodes, which were then assembled using Swagelok cells for testing. The mass loadings of the active materials are approximately $1.5 \sim 2 \text{ mg cm}^{-2}$.

In the electrode testing, a Hg/HgO electrode reference electrode was utilized in a 6M KOH aqueous solution. The specific capacity of the electrodes was calculated from the discharge curves using the following equation:

$$Q = \frac{I \times \Delta t}{3.6 \times m} \tag{1}$$

Where Q (mAh g⁻¹) represents the specific capacity based on the mass of the active materials, I (A) and Δt denote the constant charge/discharge current and discharge time measured in seconds; meanwhile, m (g) and ΔV represent the mass of the active materials and the potential window (V). The ion diffusion coefficient is calculated according to the following equation:

$$i(v) = a \times v^b \tag{2}$$

$$i(V) = k_1 v + k_2 v^{\frac{1}{2}} \tag{3}$$

Where i represents the current density, V denotes the scanning rate and potential, and b is a critical metric for evaluating charge-storage kinetics. Additionally, these represent surface-controlled and diffusion-controlled processes, respectively.

For hybrid supercapacitors, the positive electrode material consists of NiCoLDH@NPC, while the negative electrode was the wheat straw-derived porous carbon reported in our previous work¹. The mass ratio of the positive electrode to the negative electrode is approximately 1:2, as determined by charge balance theory in conjunction with the actual testing conditions. The device was evaluated in a 6 M KOH aqueous solution. The specific capacity of the device was calculated from the discharge curves using the following equation:

$$C = \frac{I \times \Delta t}{M \times \Delta V} \tag{4}$$

Where C (F g^{-1}) represents the specific capacitance based on the total mass of active materials, M (g) represents the total mass of the positive and negative active materials.

The energy density (E, Wh kg-1) and power density (P, W kg-1) are calculated by equations:

$$E = \int_{t1}^{t2} \frac{I}{3.6 \times M} \times U \, dt \tag{5}$$

$$P = \frac{3600 \times E}{\Delta t} \tag{6}$$

Where U (V) denotes the working voltage, and t_1 (s) and t_2 (s) indicate the start and end times of the discharge process, respectively.

In the case of the alkaline aqueous zinc-ion battery, the device was assembled using the NiCoLDH@NPC electrode as the cathode, a zinc foil (thickness: $150 \mu m$) as the anode, and a ZnO-saturated 6M KOH solution as the electrolyte. The energy density of the cathode is calculated using Equation (4), in which M represents the mass of the active cathode materials.

2. DFT calculation

Theoretical calculations of the structure optimization and density of states (DOS) were performed using the Vienna Ab-Initio Simulation Package (VASP) ^[10.1016/0927-0256(96)00008-0, 10.1103/PhysRevB.54,11169]. The projector augmented plane wave (PAW) pseudo potential basis set and generalized gradient approximation (GGA) functional by the PBE ^{10.1103/PhysRevLett.77.3865, 10.1103/PhysRevLett.78.1396]} parametrization was employed in these calculations. DFT+U method was also introduced to describe the electronic properties of samples, and the value of U for cobalt, and nickel are 5.5, and 3.5, respectively. A kinetic energy cutoff of 480 eV for the plane wave expansion is used for all systems. Due to existence of transition metal atom, all calculations were spin polarized. After optimization of lattice structure, for better accuracy, self-consistent field calculation was used in the extraction of band structure and density of states (DOS). In order to study the nature of the conduction and valance bands in the band structure, we have observed the projected density of states (PDOS) of each element. The

adsorbed structure and corresponding adsorb energy of two different carbon materials on the surface of LDH were also calculated. The adsorbed structures were optimized with the same parameters as above. The adsorb energies were calculated by using the following equation:

Eads = E(adsorbate/LDH) - E(adsorbate) - E(LDH)(7)



Figure S1. Morphologies of (a,b) NiCoLDH@NPC-L and (c,d) NiCoLDH NiCoLDH@NPC-M.



Figure S2. TEM images of NiCoLDH.



Figure S3. Contact angle measurements of (a) NPC and (b) YP50.



Figure S4. Nitrogen adsorption/desorption isotherms of (a) NiCoLDH@NPC-L and

(b) NiCoLDH@NPC-M.



Figure S5. Thermogravimetric analysis of NPC, NiCoLDH and NiCoLDH@NPC.



Figure S6. (a) CV curves and (b) GCD curves of NiCoLDH.



Figure S7. (a,d) CV curves, (b,e) GCD curves and (c,f) rate performances of NiCoLDH@NPC-L and NiCoLDH@NPC-M.



Figure S8. CV curves at low scan rates of (a) NiCoLDH and (b) NiCoLDH@NPC.



Figure S9. CV curves of NiCoLDH@NPC//AC device at different potential windows.



Figure S10. (a) GCD curves of NiCoLDH@NPC//AC device, (b) CV curves and (c)

GCD curves of NiCoLDH//AC device.



Figure S11. SEM images of (a) NiCoLDH electrode and (a) NiCoLDH@NPC electrode after 10000 charge-discharge cycles. (c) XRD patterns of NiCoLDH@NPC and the electrode after 10000 charge-discharge cycles.



Figure S12. (a) CV curves and (b) Nyquist plot of Zn//NiCoLDH@NPC device.

References

1. Y. Li, L. Ni, J. Luo, L. Zhu, X. Zhang, H. Li, I. Zada, J. Yu, S. Zhu, K. Lian, Y. Li and D. Zhang, *Advanced Functional Materials*, 2024, **34**, 2403448.