Supplementary Information

Rapid synthesis of MnS/NiCo-LDH heterostructure for high-performance supercapacitor

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Experimental Sections

Materials

Manganese chloride tetrahydrate ($MnCl_2.4H_2O$), Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), Nickel chloride hexahydrate ($NiCl_2.6H_2O$), Thiourea ($CS(NH_4)_2$), Potassium hydroxide pellets (KOH) and Ethanol (C_2H_5OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. The chemicals were used directly without further purifications.

Preparation of electrodes

Preparation of MnS: MnS was prepared by cyclic voltammetry electrochemical deposition with an electrochemical workstation (CHI 660E). Ni foam (1 × 2 cm) was rinsed separately with HCI, acetone, and deionized (DI) water for 20 min to eliminate impurities. In a typical synthesis, 0.198g of $MnCl_2$ and 2.855g of CH_4N_2S were dissolved in 50 mL DI water for electrodeposition. The electrodeposition was carried out at $5mV{\cdot}s^{-1}$ for 3 cycles within a potential between −1.2 - 0.2V. The MnS electrode was disposed with anhydrous alcohol repeatedly to get rid of the loosely bounded materials and it was then left to dry at 60°C overnight. The mass loading of MnS was about 1.1mg. The whole electrodeposition processes were described through the reactions below:

$$2H_2O + 2e^- = 2OH^- + H_2 \quad \text{(S1)}$$

$$SC(NH_2)_2 + 2OH^- = S^{2-} + OC(NH_2)_2 + H_2O \quad \text{(S2)}$$

$$Mn^{2+} + S^{2-} = MnS \quad \text{(S3)}$$

Preparation of MnS/NiCo-LDH: 0.291g $Co(NO_3)_2{\cdot}6H_2O$ and 0.145g $NiCl_2{\cdot}6H_2O$ were dissolved in 50 mL DI water to make the electrolyte. The deposition was also performed by cyclic voltammetry at $5mV{\cdot}s^{-1}$ scan rate for 4 cycles with a potential between −1.2 to 0.2V. Then disposed with anhydrous alcohol repeatedly, the prepared material was dried at 60°C overnight. The mass loading of MnS/NiCo-LDH was about 2.7mg. Afterwards, we converted MnS to clean nickel foam and made NiCo-LDH using the same procedure. The reactions were described by the following:

$$NO_3^- + 7H_2O + 8e^- = NH_4^+ + 10OH^- \quad \text{(S4)}$$

$$Ni^{2+} + 2OH^- = Ni(OH)_2 \quad \text{(S5)}$$

$$Co^{2+} + 2OH^- = Co(OH)_2 \quad \text{(S6)}$$

Characterization techniques

The crystalline phases were analyzed by X-ray diffraction (XRD, Miniflex-600) in the 2θ = 10-80° at 2° min^{-1}. The microstructures were viewed by scanning electron microscope (SEM, ZEISS Gemini 300) and transmission electron microscope (TEM, FEI Talos F200X). X-ray photoelectron spectrometer (XPS, Thermo Scientific) was operated to interpret the elemental valence distribution. Electrochemical performances were performed in a three-electrode system with an electrochemical workstation (CHI660E) in 2 M KOH by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), Electrochemical impedance spectroscopy (EIS) and cycling tests, the prepared electrodes as working, Pt plate as counter and Ag/AgCl as reference electrodes. The specific capacitance C_m ($F \cdot g^{-1}$) can be gained by using the formulas below:

$$C_m = \frac{I\Delta t}{m\Delta v} \tag{S7}$$

where I ($A \cdot g^{-1}$) and Δt (s) are the discharging current and time, m (g) is the active mass, and ΔV (V) is the potential.

Fabrication of ASC

A MnS/NiCo-LDH//CC ASC device was constructed applying MnS/NiCo-LDH (cathode), carbon electrode (anode) and 2 M KOH (electrolyte). The cellulose paper was used to separate two electrodes. The carbon electrode was formed by active carbon (AC), acetylene black and polytetrafluoroethylene (PTFE) (mass ratio = 8:1:1) in DI water. The MnS/NiCo-LDH and carbon electrode were balanced by the relationship below:

$$\frac{m^+}{m^-} = \frac{C_m^- \times \Delta V^-}{C_m^+ \times \Delta V^+} \tag{S8}$$

The power density (P) and energy density (E) are gained as follows:

$$E = \frac{1}{7.2} C_m V^2 \tag{S9}$$

$$P = \frac{3600 \times E}{t} \tag{S10}$$

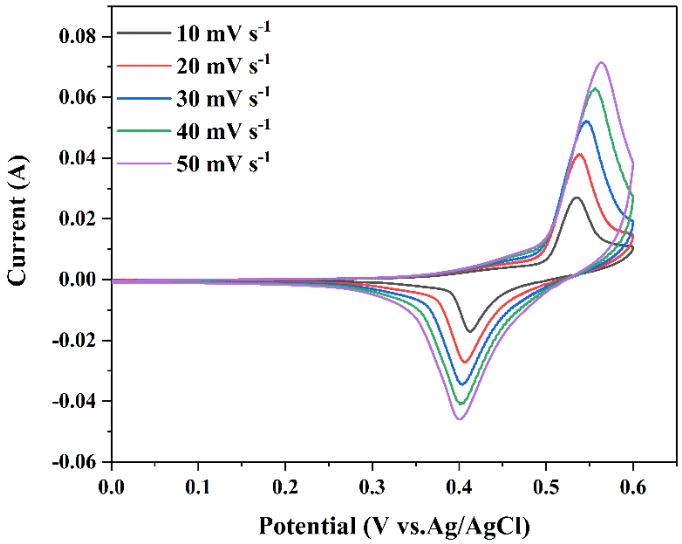

Fig. S1. CV plots of MnS at various scan rates.

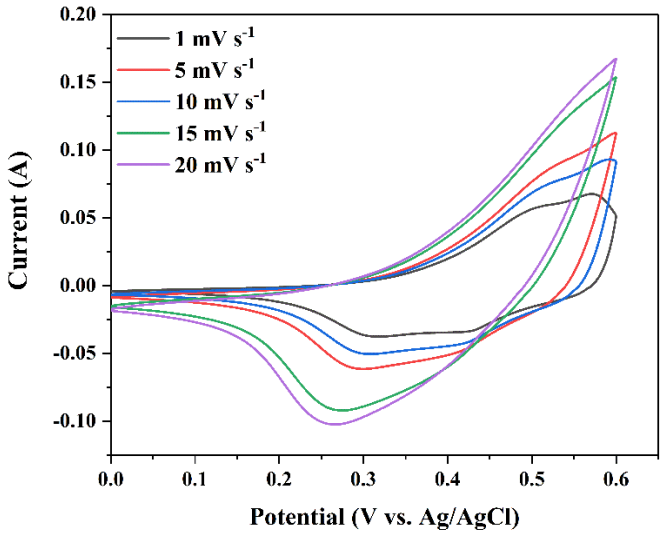

Fig. S2. CV plots of NiCo-LDH at various scan rates.

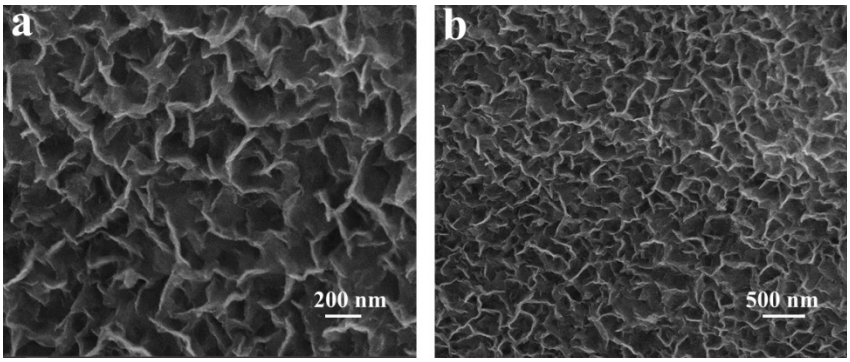

Fig. S3. (a, b) SEM images of NiCo-LDH removed from asymmetric supercapacitor after 5000 cycles