Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

A VO_3^--induced S^{2-} Exchanging Strategy to Controllably Construct Sub-nano Sulfide Functionalized Layered Double Hydroxide for Enhanced Supercapacitor Performances

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Experimental Section

Materials characterization. The surface morphology and micro-structure of the samples are studied by scanning electron microscopy (SEM, Zeiss merlin) and transmission electron microscopy (TEM, FEI Tecnai G^2 F20). The phase and crystal structure are characterized by X-ray diffraction (XRD, Rigaku D-MAX2500/PC) with Cu-Kα radiation (λ = 1.5418 Å), and the elemental composition and valence states are studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific 250xl). The N_2 adsorption-desorption isotherms at 77 K are tested by a Quantachrome instruments version 4.01.

Electrochemical test. All electrochemical tests are carried out in an electrolyte solution of 6M KOH at room temperature. The three-electrode test system consists of a working electrode, a Pt wire counter electrode, and a Hg/HgO reference electrode. The working electrode is prepared by mixing the active material, carbon black, and PTFE (5%) with a mass ratio of 8:1:1 in a small amount of ethanol, and then the mixture is dried overnight in a vacuum at 60℃. Finally, 2.5 mg of the solidified mixture is applied between two pieces of nickel foam (loading area: 1×1 cm^2) and pressed at 10 MPa for 5 s. The fabrication process of the active carbon negative electrode is similar to the working electrode, but the S-CNV-LDH is replaced by the equal quality of active carbon. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests are carried out in the electrochemical workstation (DONGHUA DH7000).

The capacity contribution rate can be calculated by formula (1) according to the CV curves.

$$i = i_{cap} + i_{diff} = k_1 v + k_2 v^{1/2} \quad \text{.....(1)}$$

where i is the current at a certain voltage, $k_1 v$ represents the capacitance contribution response current, $k_2 v^{1/2}$ represents the diffusion contribution response current.

The specific capacity (F g^{-1}) can be calculated from formula (2) according to GCD curves.

$$C = \frac{I\,\Delta t}{m\,\Delta V} \quad \text{.....(2)}$$

where I (mA) is the current, m (mg) is the mass of active materials, Δt (s) is the discharge time of the electrodes at related current density, and ΔV (V) is the voltage window.

The negative and positive electrodes of asymmetric supercapacitor device S-CNV-LDH//AC are matched following the formula (3)

$$C_+ m_+ \Delta V_+ = C_- m_- \Delta V_- \quad \text{.....(3)}$$

where C_+ and C_- are the capacitance of positive and negative electrode, m_+ and m_- are the mass of positive and negative electrode, ΔV_+ and ΔV_- are the voltage window of positive and negative electrode, respectively.

The energy density (Wh kg^{-1}) and power density (W kg^{-1}) are calculated by the formula (4) and (5) respectively，

$$E = \frac{1}{7.2} C\,\Delta V^2 \quad \text{.....(4)}$$

$$P = 3600\frac{E}{\Delta t} \quad \text{.....(5)}$$

where C (F g^{-1}) is the specific capacity, ΔV (V) is the voltage window, and Δt (s) is discharge time.

Supplementary Figures

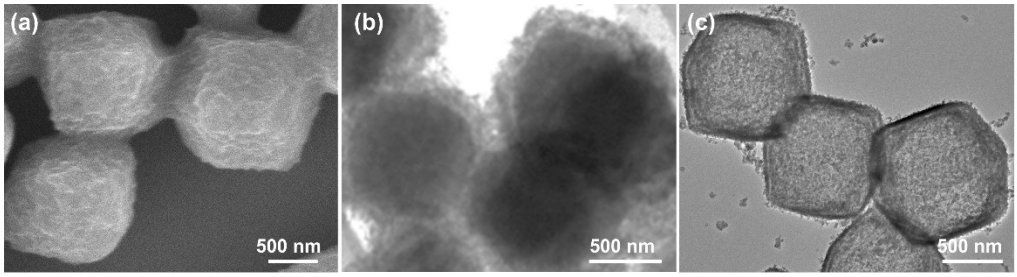

Fig. S1 The SEM image (a) and TEM image (b) of ZIF-67@Co/Ni LDH, the TEM image of V-CN-LDH.

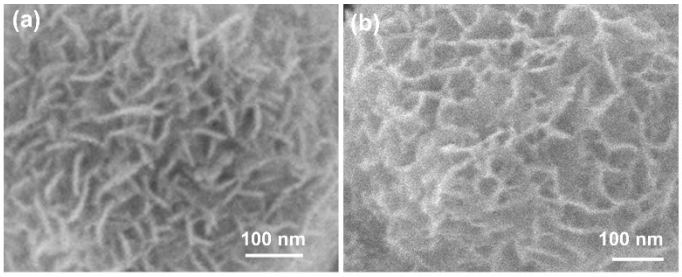

Fig. S2 The enlarged SEM images of V-CN-LDH (a) and S-CNV-LDH (b)

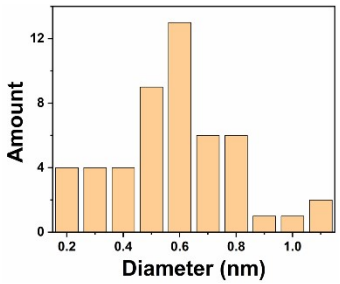

Fig. S3 Frequency histogram of size of $(Ni/Co)_{1-x}S$ sub-nanoparticle.

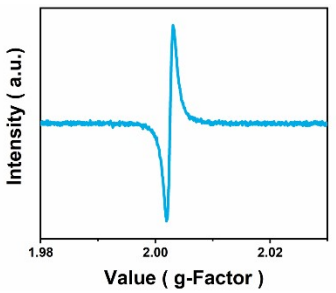

Fig. S4 EPR spectra of S-CNV-LDH

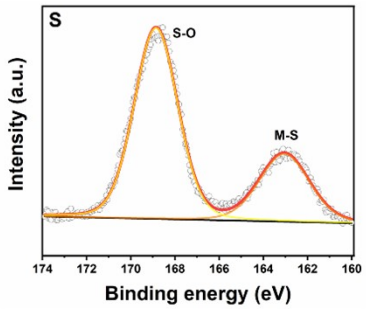

Fig. S5 The XPS spectra of S and Na spectrum of S-CNV-LDH nanocage.

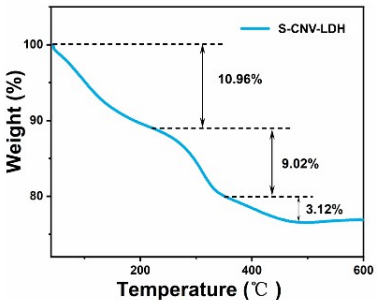

Fig. S6 The TGA curve of S-CNV-LDH nanocage.

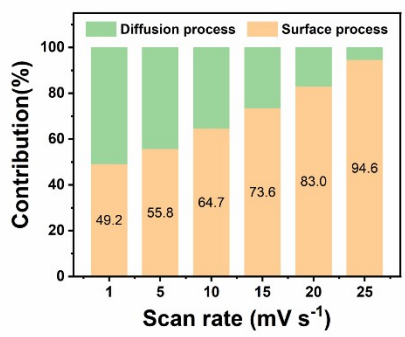

Fig. S7 The contribution ratio between surface and diffusion-controlled process of S-CNV-LDH at different scan rate.

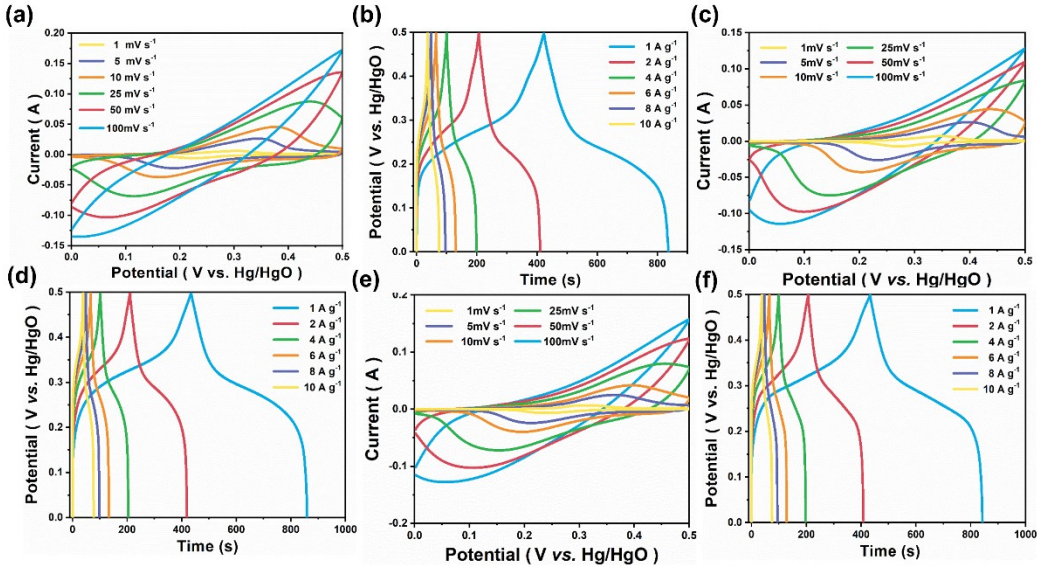

Fig. S8 The CV curve and GCD curve of V-CN-LDH-50 (a, b), V-CN-LDH-90 (c, d), V-CN-LDH-110 (e, f).

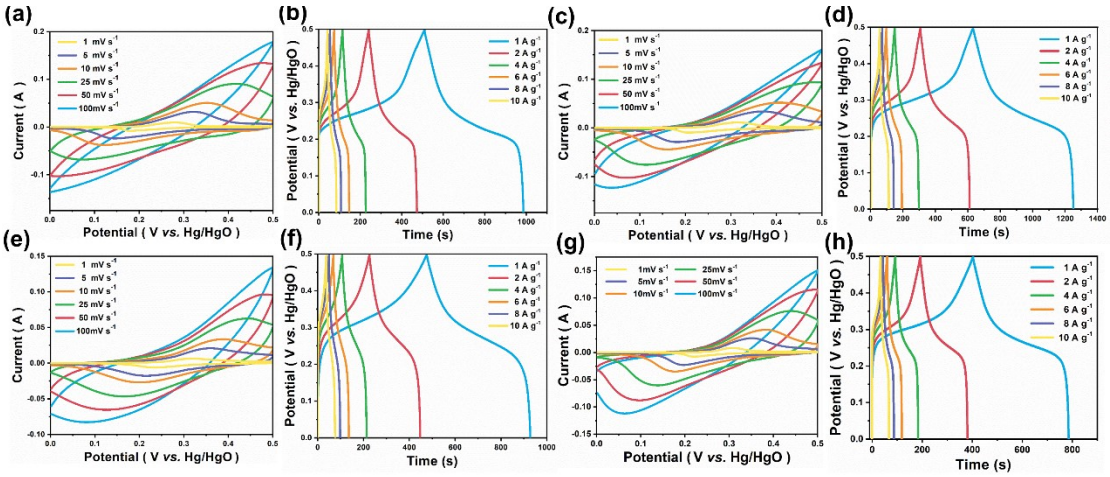

Fig. S9 The CV curve and GCD curve of S-CNV-LDH-100 (a, b), S-CNV-LDH-150 (c, d), S-CNV-LDH-250 (e, f) and S-CNV-LDH-300 (g, h).

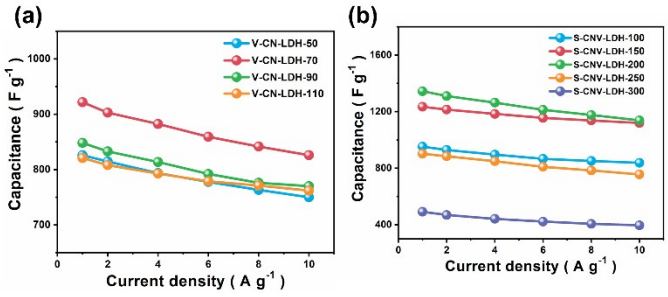

Fig. S10 The specific capacitance values of V-CN-LDH (a), S-CNV-LDH (b) nanocages at different current densities.

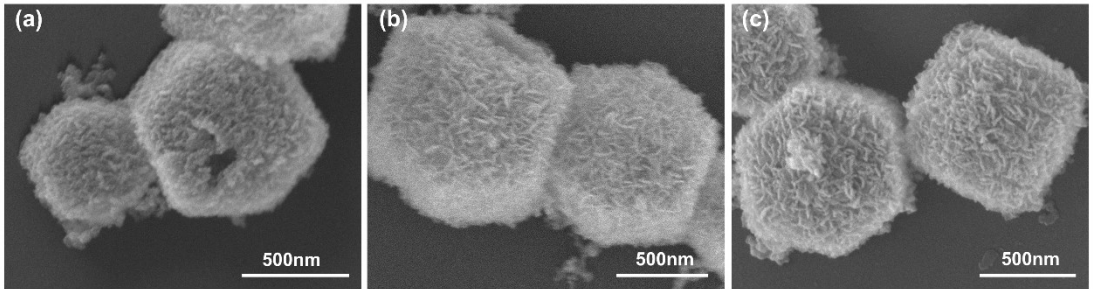

Fig. S11 The SEM images of V-CN-LDH-50 (a), V-CN-LDH-90 (b) and V-CN-LDH-110 (c).

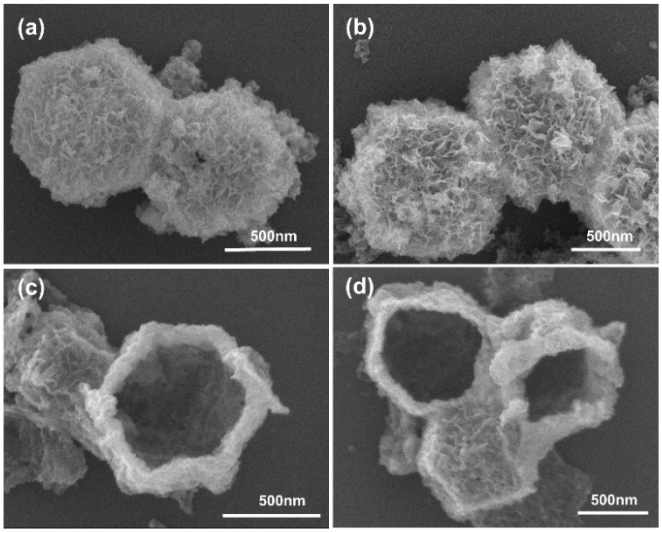

Fig. S12 The SEM images of S-CNV-LDH-100 (a), S-CNV-LDH-150 (b), S-CNV-LDH-250 (c) and S-CNV-LDH-300 (d).

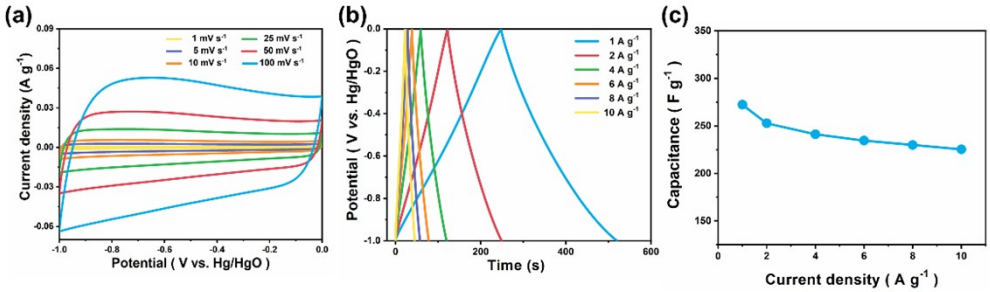

Fig. S13 The CV curve (a), GCD curve (b) and specific capacitance values of AC (load mass is 2 mg).

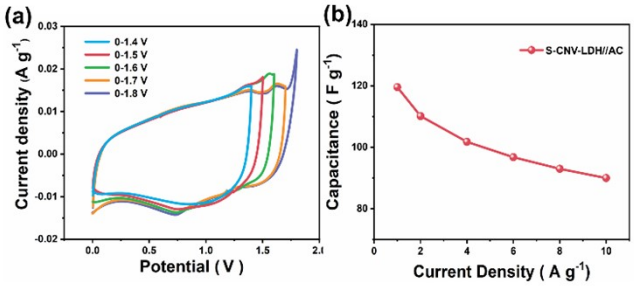

Fig. S14 The CV curve (a) at different scan rates and the specific capacitance values (b) of S-CNV-LDH.

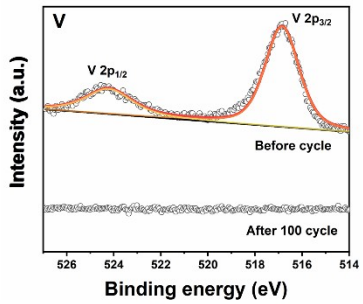

Fig. S15 XPS spectra of V spectrum of S-CNV-LDH.

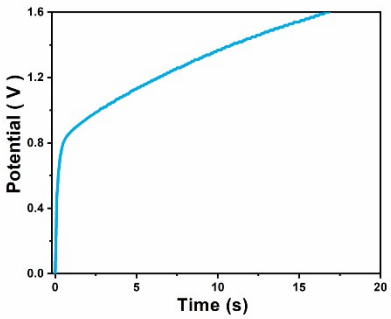

Fig. S16 Charging diagram of S-CNV-LDH//AC at the current density of 10 A g^{-1}.

Supplementary Tables

Tab.S1 The content of element in V-CN-LDH and S-CNV-LDH

Element	V-CN-LDH	S-CNV-LDH
Co (%)	44.1	42.3
Ni (%)	35.9	34.6
V (%)	20.0	11.5
S (%)	0	11.6

Tab. S2 Parameters of the proposed equivalent circuit model.

Materials	$R_s(\Omega)$	CPE1-T	CPE1-P	$R_{ct}(\Omega)$	W-R(Ω)	W-T	W-P
V-CN-LDH	0.747	0.012	0.828	1.043	5.000	1.902	0.430
S-CNV-LDH	0.571	0.008	0.848	0.877	3.728	1.503	0.444

Tab. S3 Comparison of NC//FG ASC Device Performance with the Other Works

Materials	Power density ($kW\ kg^{-1}$)	Energy density ($W\ h\ kg^{-1}$)	Ref.
$NiCo_2S_4$//AC	3.8	23.4	[61]
CoV_2O_6/CNTs//AC	0.8	13.8	[62]
NiCoS@PPy//AC	0.8	34.4	[63]
NiCoS/CC//AC	0.4	40.0	[64]
ZnCoS/NF//AC/NF	8.5	22.7	[65]
N-DLCHs//$CuCo_2S_4$	8.3	20.3	[66]
NiS/PVA-$LiClO_4$//NiS	1.2	15.0	[67]
$NiCo_2S_4$-rGO//NCCF-rGO	1.6	36.0	[68]
$MnCo_2S_4$//rGO	0.8	31.3	[69]
$NiCo_2S_4$/Co_9S_8//AC	3.8	17.5	[70]
$Cu_{1.8}S$-Ni_3S_2@NF-60//AC	7.9	30.9	[71]
NiCo LDHs@PANI@CC//AC	0.8	26.5	[72]
HC@NiCo LDHs//AC	0.8	11.7	[73]
NiCo-LDH@PANI@CC//AC	6.4	8.2	[74]
S-CNV-LDH//AC	0.8	42.5	This work