Supplementary Information

3D nanoflower-like MoSe₂ encapsulated with hierarchically

anisotropic carbon architecture: A new and free-standing anode with

ultra-high areal capacitance for asymmetric supercapacitors

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1. Experimental Section

Preparation of delignified wood (DW): The balsa wood blocks were sliced into 1.5 mm thickness sheets perpendicular to the direction of vessels, and then the sheets were immersed into a mixed aqueous solution of 1.25 M sodium hydroxide and 0.2 M sodium sulfite at 100 °C for 5 h. The chemical waste liquid was poured out and deionized water was added at 100 °C for 0.5 h several times. Finally, the samples were dried by vacuum freezing for 24 h.

Preparation of 3D MoSe₂ nanoflowers@CDW (3D MoSe₂ NFs@CDW) anode: 12 mmol selenium powder was dissolved in 15 mL NaBH₄ (0.2 g) aqueous solution, and 5 mmol sodium molybdate was dissolved in 60 mL deionized water with magnetic stirring for 30 min, respectively. Then, the above two solutions were mixed by stirring intensely, till forming a homogeneous reddish-brown solution. The obtained mixture was transferred into a 100 mL sealed Teflon autoclave and heated at 200 °C for 24 h. The product (MoSe₂) was collected and washed with distilled water several times, then dried in a vacuum oven at 60 °C for 12 h. The preparation of 3D MoSe₂ NFs@CDW follows a combined method of ultrasound-assisted assembly and carbonization, whose procedures can be described as follows: 2.5 mg mL⁻¹ MoSe₂ aqueous suspension was prepared by ultrasonic treatment with an output power of 500 W in an ice water bath for 1h. The DW sheets were soaked in the suspension and then underwent an ultrasonic treatment at the same condition for 5 min. After removing unreacted Se and drying, the 3D MoSe₂ NFs@DW was heated at 500 °C for 1 h and then carbonized at 800 °C for 2 h under N₂ atmosphere in a tube furnace. All of the heating rate during the carbonization is 5 °C min⁻¹ and the N₂ flow rate is 100 sccm. The as-prepared self-supported 3D MoSe₂ NFs@CDW directly acted as an anode with an exposed geometric area of 1×1 cm².

Preparation of MnO₂@CDW cathode: The fabrication of MnO₂@CDW cathode was conducted according to the following procedures.^{\$1} Briefly, DW was firstly used as raw material to obtain CDW via a carbonization process, and the carbonization parameters are consistent with those of the preceding text (i.e., heating at 500 °C for 1 h and then carbonizing at 800 °C for 2 h under N₂ atmosphere; the heating rate is 5 °C min⁻¹ and the N₂ flow rate is 100 sccm). Then, the resulting CDW was completely immersed in a 50 mL KMnO₄ solution. The mass ratio of KMnO₄ to CDW is set as 1:4, which has been confirmed elsewhere to contribute to acquiring favorable electrochemical property for composites consisting of MnO₂ and carbon.^{\$2} The mixture was heated at 60 °C for 12 h. After the heating, the sample was rinsed with a great deal of deionized water and finally dried at 60 °C for 24 h in vacuum oven. The as-prepared and self-supported 3D MnO₂@CDW directly served as a cathode with an exposed geometric area of 1 × 1 cm².

Characterization

Morphology was characterized by using transmission electron microscope (TEM) (FEI, Tecnai G2 F20) and scanning electron microscope (SEM) (Hitachi, S4800) equipped with an energy-dispersive X-ray (EDX) detector for elemental analysis. Pore structure and surface area were analysed by N_2 adsorption–desorption tests by an accelerated surface area and porosimeter system (3H-2000PS2 unit, Beishide Instrument S&T Co., Ltd). Thermal stability was studied by a TA Q600TG analyzer from room temperature to 800 °C with a heating rate of 5 °C min⁻¹ under nitrogen atmosphere. X-ray diffraction (XRD) analysis was implemented on a Bruker D8 Advance TXS XRD instrument with Cu K α (target) radiation ($\lambda = 1.5418$ Å) at a scan rate (2θ) of 4° min⁻¹ and a scan range from 5 to 85°. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Escalab 250Xi system by using a spectrometer with a dual Al Ka X–ray source. Deconvolution of overlapping peaks was conducted via a mixed Gaussian–Lorentzian fitting program (Origin 9.0, Originlab Corporation).

Electrochemical Characterization

Electrochemical tests of the as-prepared electrodes, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS), were conducted at room temperature in three-electrode setup by using a CS350 electrochemical workstation (Wuhan CorrTest Instruments Co., Ltd, China). In the aqueous electrolyte of 3 M KOH, a Pt sheet electrode and a Hg/HgO electrode served as the counter and reference electrodes, respectively. The exposed geometric area of the working electrode is equal to 1×1 cm². The CV curves for 3D MoSe₂ NFs@CDW and CDW were recorded at various scan rates (5, 10, 20 50 and 100 mV s⁻¹) in a potential range from 0 to -0.8 V and the GCD curves were obtained at various current densities $(1, 2, 5, 10 \text{ and } 20 \text{ mA cm}^{-2})$ in a potential window from -0.3to -0.8 V. For MnO₂@CDW electrode, the CV curves were recorded at various scan rates (5, 10, 20, 50 and 100 mV s⁻¹) in a potential range from 0 to 0.8 V and the GCD curves were obtained at various current densities of 0.2, 0.5, 1, 2 and 5 mA cm⁻² in a potential window from 0 to 0.5 V. The EIS measurements of all the samples were carried out in the frequency range of 0.01 Hz to 100 kHz with an alternate current amplitude of 5 mV. To achieve the reliable statistic of electrochemical measurements, the electrodes were firstly activated through 100 times of CV tests at 100 mV s⁻¹.

Device fabrication: the 3D MoSe₂ NFs@CDW anode and MnO₂@CDW cathode were used to assemble an asymmetric supercapacitor (ASC) with a piece of cellulose paper as the separator and gold foils as the collectors, and then the device was soaked into the aqueous electrolyte of 3 M KOH at room temperature for two-electrode system tests. Two ASC devices in series were charged about 7 s up to 3.2 V at the current density of 40 mA cm⁻² in the aqueous electrolyte of 3 M KOH, and were subsequently connected to the circuit containing a blue LED (2.5 V) as the power supply. Since the circuit was closed, LED was lighted up and the lighting time lasted about 45 s.

Calculations: For the CDW, 3D MoSe₂ NFs@CDW and MnO₂@CDW electrodes and the assembled ASC device, the areal (C_s , F cm⁻²) or gravimetric (C_m , F g⁻¹) specific capacitances are calculated from GCD curves at different current densities according to following equations:

$$C_{\rm s} = I\Delta t \,/\, s\Delta V \text{ or } C_{\rm m} I\Delta t \,/\, m\Delta V \tag{1}$$

where I, Δt , and ΔV refer to the discharge current (mA), discharge time (s) and potential window (V), respectively; *s* and *m* represent the specific area (cm²) and mass (mg) of electrodes, respectively. For the ASC device, *m* (mg) is the total mass of both cathode and anode (i.e., 9.88 mg cm⁻²).

The areal energy density (E_s) and areal power density (P_s) are evaluated on the basis of capacitance values:

$$E_{\rm s} = \frac{1}{2} C_{\rm s} (\Delta V)^2 / 3600 \tag{2}$$

$$P_{\rm s} = \frac{E_{\rm s}}{\Delta t} \times 3600 \tag{3}$$



2. N₂ adsorption-desorption isotherms of CDW and 3D MoSe₂ NFs@CDW

Figure S1. N₂ adsorption-desorption isotherms of CDW and 3D MoSe₂ NFs@CDW.

The pore structure is studied by N₂ adsorption–desorption experiments, and the specific surface area is calculated by the Brunauer–Emmet–Teller (BET) method. As shown in Fig. S1, both CDW and 3D MoSe₂ NFs@CDW display type-IV adsorption isotherm according to the IUPAC classification, and the hysteresis loop between the adsorption and desorption isotherms is attributed to the capillary condensation occurring in the mesopores. The drastic increase of adsorption uptake in the initial stage indicates the existence of micropores. CDW achieves a high specific surface area of 269 m² g⁻¹. The introduction of CDW endows 3D MoSe₂ NFs@CDW with a specific surface area of 223 m² g⁻¹. As a result, based on the proportions of CDW and MoSe₂ in the 3D MoSe₂ NFs@CDW composite (namely 75.2 wt.% and 24.8 wt.%, the calculation is available in later section 6), the specific surface area of 3D MoSe₂ NFs g⁻¹.

3. SEM image of scanning region for elemental mappings



Figure S2. SEM image of scanning region for elemental mappings.

4. Longitudinal-section SEM image of CDW



Figure S3. Longitudinal-section SEM image of CDW.

5. Formation mechanism of 3D $MoSe_2 NFs$



Figure S4. Formation mechanism of 3D MoSe₂ NFs in a hydrothermal condition.





Figure S5. Thermogravimetric curves of CDW and 3D MoSe₂ NFs@CDW.

The thermogravimetric curves of CDW and 3D MoSe₂ NFs@CDW are shown in Fig. S5, where their residual weights at 800 °C are around 92.70% and 94.51%, respectively. MoSe₂ is a thermally stable material with a high melting point of 1200 °C, and thus the weight loss during the pyrolysis is primarily ascribed to the residual oxygen-containing components in CDW. As a result, the carbon proportion in the composite (namely 3D MoSe₂ NFs@CDW) can be roughly calculated as (1-94.51%)/(1-92.70%) = 75.2 wt.%. Therefore, the content of MoSe₂ is 24.8 wt.% in 3D MoSe₂ NFs@CDW.

7. XRD and XPS analysis of 3D MoSe₂ NFs@CDW



Figure S6. Crystal structure and elemental valences of 3D MoSe₂ NFs@CDW.

(a) XRD patterns and powder diffraction standard pattern of MoSe₂ (JCPDS card no. 29–0914); XPS spectra of (b) survey, (c) Mo 3d and (d) Se 3d.

8. XPS C 1s spectrum of 3D MoSe₂ NFs@CDW



Figure S7. XPS C 1s spectrum of 3D MoSe₂ NFs@CDW.

9. CV and GCD curves of CDW



Figure S8. (a) CV curves of CDW at various scan rates ranging from 5 to 100 mV s⁻¹,
(b) GCD curves of CDW at various current densities ranging from 1 to 20 mA cm⁻².

Figure S8a displays the CV curves of CDW under the potential from -0.8 to 0 V at various scan rates ranging from 5 to 100 mV s⁻¹. The CV profiles is heavily distorted from the rectangular shape, which is attributable to faradaic reactions that occur on the surface of CDW electrode, such as reactions between the carbonyl (C=O) and hydroxyl (C-OH) groups, i.e., C=O + H⁺ + e⁻ \rightarrow C-OH.^{S3} GCD curves of CDW at various current densities are presented in Figure S8b, where a capacitance value of 584 mF cm⁻² is achieved at 1 mA cm⁻² and decreases to 128 mF cm⁻² at 20 mA cm⁻².

10. GCD curves of 3D MoSe₂ NFs@CDW for first and last five cycles



Figure S9. Cycling stability tests for 3D MoSe₂ NFs@CDW showing (a) first five cycles and (b) last five cycles.





Figure S10. Electrochemical property of MnO₂@CDW cathode. (a) CV curves at various scan rates ranging from 5 to 100 mV s⁻¹; (b) GCD curves at various current densities from 0.2 to 5 mA cm⁻²; (c) areal and gravimetric specific capacitance at different current densities calculated by GCD, the areal specific capacitance values are about 215, 168, 132, 96 and 48 mF cm⁻² at 0.2, 0.5, 1, 2 and 5 mA cm⁻², corresponding to the gravimetric specific capacitance values of 48, 38, 30, 22 and 11 F g⁻¹, respectively; (d) Nyquist plots; (e) the coulombic efficiency is in almost stable level (~100%) during the 5000 GCD cycles at 5 mA cm⁻², and the capacitance retains 91.3% of the original value after the cycles; (f) GCD curves for first and last five cycles.

12. Table S1: Electrochemical property comparison of 3D MoSe₂ NFs@CDW

Table S1. A real specific capacitance comparison of 3D MoSe₂ NFs@CDW with

Electrodes	Areal capacitance (mF cm ⁻²)	Electrolyte	Ref. ^a
3D porous MoS ₂	33 (25.5 mA cm ⁻²)	0.5 M H ₂ SO ₄	20a
h-WO ₃ /WS ₂ nanowire	47.5 (5 mV s ⁻¹)	0.1 M Na ₂ SO ₄	20b
MoS _x thin-film-coated carbon fiber paper	83.9 (5 mV s ⁻¹)	0.5 M H ₂ SO ₄	20c
N-doped 1T-2H MoSe ₂ /graphene	136 (4 mV s ⁻¹)	0.5 M H ₂ SO ₄	20d
Porous reduced graphene oxide films	71 (1 mA cm ⁻²)	1.0 M H ₂ SO ₄	21a
Carbon cloth	88 (10 mV s ⁻¹)	1.0 M H ₂ SO ₄	21b
Graphene foam/CNTs/PPy	400 (5 mV s ⁻¹)	0.5 M Na ₂ SO ₄	21c
Graphite foam-CNT@Fe ₂ O ₃	659.5 (5 mA cm ⁻²)	2.0 M KOH	21d
3D MoSe ₂ NFs@CDW	1043 (1 mA cm ⁻²)	3.0 M KOH	This work

typical TMD-based electrodes and some other anode materials.

^{*a*}Please find these references in the main body of the paper.

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Devices	Type	Maximum areal energy density (μW h cm ⁻²)	Areal capacitance (mF cm ⁻²)	Potential range (V)	Electrolyte	Ref
RuO ₂ /PEDOT:PSS//PEDOT:PSS	ASC	0.53 (150 μW cm ⁻²)	1.06 (50 mV s ⁻¹)	0-1.2	PVA/H ₂ SO ₄	S4
MoSe ₂ coated stainless	SSC	10.5 (270 μW cm ⁻²)	18.93 (0.5 mA cm ⁻²)	0-2.0	PVDF/NaNbO ₃	SS
Cu ₂ O/Cu/graphite/cellulose paper//carbon paper	ASC	~11 (400 μW cm ⁻²)	122 (1 mA cm ⁻²)	0-0.8	6M KOH	S6
MnO ₂ /CDCCª//CDCC	ASC	${\sim}30~(150~\mu{W}~cm^{-2})$	96.3 (0.2 mA cm ⁻²)	0-1.5	$1 \mathrm{M} \mathrm{Na}_2 \mathrm{SO}_4$	S1
Ni(OH) ₂ -N-doped graphene//N-doped graphene	ASC	80 (994 μW cm ⁻²)	255 (1 mA cm ⁻²)	0-1.45	H ₂ SO ₄ -PVA	S7
CoMn–LDH ^b //porous carbon	ASC	96 (1500 μW cm ⁻²)	308.48 (2 mA cm ⁻²)	0-1.5	1M K aOH	S8
3D MoSe ₂ NFs@CDW//MnO ₂ @CDW	ASC	147 (2000 μW cm ⁻²)	415 (2.5 mA cm ⁻²)	0-1.6	3 M KOH	This work
^{<i>a</i>} CDCC: cotton-derived carbon cloth; b Co	Mn-LDH: (Oobalt-manganese layered do	uble hydroxide; °VOS:	ulfur-doped V ₆ O ₁	3-x	

13. Table S2: Electrochemical property comparison of ASC and SSC devices

14. Reaction equations for the formation of MoSe₂

$$2Se + 4BH_4^{-} + 7H_2O \rightarrow 2HSe^{-} + B_4O_7^{-2} + 14H_2$$
 (S1)

$$4 \operatorname{MoO}_{4}^{2-} + \operatorname{BH}_{4}^{-} + 10 \operatorname{H}_{2} \operatorname{O} \to 4 \operatorname{Mo}^{4+} + \operatorname{BO}_{2}^{-} + 24 \operatorname{OH}^{-}$$
(S2)

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-}$$
(S3)

$$Mo^{4+} + 2Se^{2-} \rightarrow MoSe_2$$
 (S4)

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