## **Supporting Information**

A facile strategy for the synthesis of three-dimensional heterostructure self-assembled MoSe<sub>2</sub> nanosheets and their application as an anode for high-energy lithium-ion hybrid capacitors

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BET SSA Pore size distribution Pore size distribution **Electrode material**  $(m^2/g)$ range (micropore) range (mesopore) Reference (nm) (nm) 1592.3 0.49-2 2-3.73 AC This work PNC-700 985 0.5-2 (70) PNC-800 1931 2-5 PNC-900 2433 2300 PNC-1000 PM-CNPs800 178.08PM-CNPs900 237.86 2-3.3 (71) \_ 125.74 PM-CNPs1000 hNCNC700 2407 hNCNC800 1794 hNCNC900 1529 0.6-2 2-11 (72) hCNC700 2392 hCNC800 1912 hCNC900 1592

**Table S1** The specific surface areas (SSA) and pore size distribution range of ACCompared to other nano-porous carbon material in the literature.



Fig. S1 CV profles of the MoSe<sub>2</sub> electrode within a cutoff voltage window of 0.01-3.0 V at a slow scan rate of 0.1 mV/s.



**Fig. S2** Kinetic analysis. Left column: MoSe<sub>2</sub> Nanoflowers (Scanning speed is in the range of 0.2-0.8 mV/s); Right column: MoSe<sub>2</sub> Nanoflowers (Scanning speed is in the range of 0.6-2.0 mV/s). (a, b) CV curves at different scan rates. (c,d) Plots of  $v^{1/2}$  vs.  $i/v^{1/2}$  used for calculating constants  $k_1$  and  $k_2$  at different potentials.

## The detailed calculation method of pseudocapacitive contribution

Following the research works of the Dunn and co-workers by using the Trasatti analysis, we can use the scan-rate-dependent CV curves (Figure S2a,b) to quantify the contribution from capacitive effects (both surface pseudocapacitance and double-layer capacitance) and diffusion-controlled Li<sup>+</sup> insertion process to the current response according to the following equation:

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

where i(V),  $k_1 v$  and  $k_2 v^{1/2}$  represent the total current response at a given potential V,

current due to surface capacitive effects, and current due to diffusion-controlled Li<sup>+</sup> insertion process, respectively. The above equation can also be reformulated as

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

By plotting  $i(V)/v^{1/2}$  vs.  $v^{1/2}$  at different potentials, one can calculate the values of  $k_1$  (slope) and  $k_2$  (intercept) from the straight lines. This allows one to quantify the fraction of the current at specific potentials to the capacitive effect and diffusion-controlled insertion one (see Figure S2c,d). After integration of the enclosed CV area, the amount of stored charge from different energy storage modes can be distinguished, expressed by the following equation:

$$Q = Q_s + Q_d \tag{3}$$

where, Q,  $Q_s$ , and  $Q_d$  represent the total stored charge included in the enclosed CV area at set scan rate, charges from surface capacitive effects, and charges from diffusion controlled Li<sup>+</sup> insertion process, respectively.<sup>68</sup> It is accepted that a higher scan rate can cause more capacitive contribution, so in Figure 4b, we calculates the contribution of pseudo-capacitance and diffusion control contribution according to CV curves of 0.6 mV/s. In Figure 4b, the potential profiles for the current responses of capacitive effects (red area) are presented to compare with the total measured current areas at a scan rate of 0.6 mV/s. At the same time, the calculated pseudocapacitive contribution at higher and lower sweep speeds is shown in Figure 4c.



**Fig. S3** Electrochemical impedance spectra of MoSe<sub>2</sub> anode is recorded at different cycle number conditions.



**Fig. S4** (a) Ex-situ XRD patterns of the MoSe<sub>2</sub> nanoflower electrode at different states during the 100th cycle. (b) The CV curve before the MoSe<sub>2</sub> electrode cycle is at a sweep rate of 0.2 mV/s. (c) Ex-situ XPS spectra of MoSe<sub>2</sub> nanoflower at full discharged (0.01 V) during the after 100 cycle. (d) Ex-situ XPS spectra of MoSe<sub>2</sub> nanoflower at fully charged (3.0 V) state during the 100 cycle.

## The detailed arguments for the claim of elemental selenium precipitation are shown in Fig. S4

In order to explain the reason why the capacity of MoSe<sub>2</sub> nanoflower electrode material is gradually increasing during the cycle of lithium-ion battery anode, we performed ex-situ XRD and ex-situ XPS tests on the assembled MoSe<sub>2</sub> button half-cell under full charge and full discharge. Firstly, we have sonicated the MoSe<sub>2</sub> electrode sheets that have been cleaned and removed to prepare a powder sample. Next, we tested the ex-situ XRD on its powder sample. As shown in Fig. S4a, it can be clearly seen that the main product after complete discharge is Li<sub>2</sub>Se (XRD diffraction peak corresponds to JCPDS No. 47-1696). When fully charged, it is mainly MoSe<sub>2</sub>, and some elemental Se is produced (XRD diffraction peak corresponds to JCPDS No. 32-092), which explains the reason for the increase in capacity during the cycle. Secondly, in order to further explain the precipitation of elemental selenium during charge and discharge, we tried an ex-situ XPS test for the removed MoSe<sub>2</sub>/Li metal half-cell electrode during the 100th cycle. As apparent in Fig. S4c, when the battery is completely discharged. In the Se 3d XPS spectra, two bands at 54.3 and 55.4 eV correspond to the  $3d_{5/2}$  and  $3d_{3/2}$ peaks of Se<sup>2-</sup> in the MoSe<sub>2</sub> electrode sheet. Conversely, when the battery is fully charged, it can be apparent from the XPS spectrum of Se3d that the original Se<sup>2-</sup> is still present. Unlike the fully discharged XPS, it has a new pair of peaks (55.0 eV and 56.30 eV) in Fig.S4d. After our peak processing and reference to the literature, it is caused by the spin-orbital split at 55.0 eV and 56.30 eV, which is attributed to the presence of metallic selenium. That is to say, the Se ions in the material undergo a valence change from -2 to 0. These results are consistent with the MoSe<sub>2</sub> lithium storage mechanism previously reported in the literature. Therefore, we can say that the MoSe<sub>2</sub>/Li metal half-cell does produce some elemental selenium during charging and discharging, which leads to an increase in capacity during the cycle.



Fig. S5 Long cycling performance of  $MoSe_2$  anode at the current density of 0.5 A/g and 1.0 A/g, respectively.



**Fig. S6** (a) CV curves of AC at various scan rates. (b) Rate performance of AC (The illustration shows the galvanostatic charging-discharging curves of AC at different current densities). (c) EIS spectra of AC cathode is recorded at different cycle number conditions. (d) Cycling performance of AC at the current density of 1.0 A/g.



**Fig. S7** CV curves of MoSe<sub>2</sub>//AC LIHCs at different scan rates range from 1 to 20 mV/s. Among them, the only difference is the potential window (a) 0.5-3.5 V. (b) 0.5-4.0 V. (c) 0.5-4.3 V. (d) 0.5-4.5 V.

## A detailed description of the failure of the organic electrolyte to decompose within this potential range is shown in Fig. S6

We can clearly see that the CV curve in Figure S6d still exhibits a curve similar to a rectangular shape at a potential window of 0.5-4.5 V, and the charging curve does not become sharply steep at a potential higher than 3.5 V, which indicates the anode and cathode of the device are stable at such a high potential, and the electrolyte did not decompose significantly at this potential. For Figure S6(b,c), the CV curve of the assembled device is similar to the curve in Figure S6d which shows that the device is also stable under the potential window of 0.5-4.0 V and 0.5-4.3 V. And the electrolyte has no obvious decomposition phenomenon. Looking back at the CV curve of the device assembled in Figure S6a, it is obvious that we can see that the device does not exhibit instability and electrolyte decomposition at both ends of the 0.5-3.5 V potential window. In summary, We believe that the lithium-ion hybrid capacitors by our assembled are essentially stable at both ends of the anode and cathode (vs.  $Li/Li^+$ ) at this potential range (0.5-3.5 V).



**Fig. S8** Electrochemical impedance spectra of MoSe<sub>2</sub>//AC LIHCs is recorded at different cycle number conditions.

**Table S2** Performance comparison results of the lithium-ion hybrid supercapacitorbased on  $MoSe_2$  anode in this work and fibrous supercapacitor reported in the literature.

Electrode	Energy storage	Electrolyte	Voltage range	Energy	Power	Cycling life	Reference
materials	device		(V)	density	density		
MoSe <sub>2</sub> //AC	Lithium-ion	LiPF <sub>6</sub>	0.5-3.5V	78.75 Wh/kg	150 W/kg	70.28%@5000	This Work
	hybrid capacitor					cycles	
CF@TiO2@	fibrous	PVA-H <sub>3</sub> PO <sub>4</sub>	0-0.8V	1.21	296.33	81%@3000	(73)
MoS <sub>2</sub>	supercapacitor			uWh/cm <sup>2</sup>	$\mu$ W/cm <sup>2</sup>	cycles	