Supplementary Material

Designing a 3D MXene Microsphere Encapsulating MOF-Derived ZnSe Nanoparticles as an Anode for Highly Stable Potassium-Ion Batteries

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Material characterization

The overall morphologies and structures of the composites were identified through field-emission scanning electron microscopy (FE-SEM, S-5000) and transmission electron microscopy (TEM, JEM-2100F, Korea Basic Science Institute (Daegu)). The crystal structures were confirmed through X-ray diffraction (XRD) conducted using Cu-Kα radiation. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific K-Alpha instrument to analyze the chemical composition of the samples. For fitting the XPS spectra, the XPSPEAK41 program was used. The surface areas of the samples were determined using the Brunauer–Emmett–Teller (BET, BELSORP-mini II, SOLETEK) method, with N_2 as the adsorption gas. Thermogravimetric analysis (TGA) was performed using a Pyris 1 TGA (Perkin Elmer) within a temperature range of 25–800 °C at a heating rate of 10 °C min^{-1} under an air atmosphere.

Electrochemical measurement

The electrochemical performance of the obtained composites was measured using a 2032-type coin cell. A slurry was prepared by mixing the composite powder, carbon black (Super P), and carboxymethyl cellulose (CMC) in a weight ratio of 7:2:1. K metal and a glass filter were used as the counter electrode and separator, respectively. The electrolyte was composed of 3.0 M KFSI dissolved in a mixture of diethylene glycol dimethyl ether. The electrodes were analyzed within a potential range of 0.01–3.0 V at various current densities to investigate their charge–discharge characteristics in the KIBs. Cyclic voltammetry (CV) was conducted at a scan rate of 0.1 mV s^{-1}. The diameter of the electrode was 11 mm and the mass loading of the active materials was 1.7 mg cm^{-2}. Electrochemical impedance spectroscopy (EIS) was conducted using a ZIVE-SP1 potentiostat with a range of 0.1–100 kHz and an AC voltage of 5 mV.

Supplementary Figures and Table

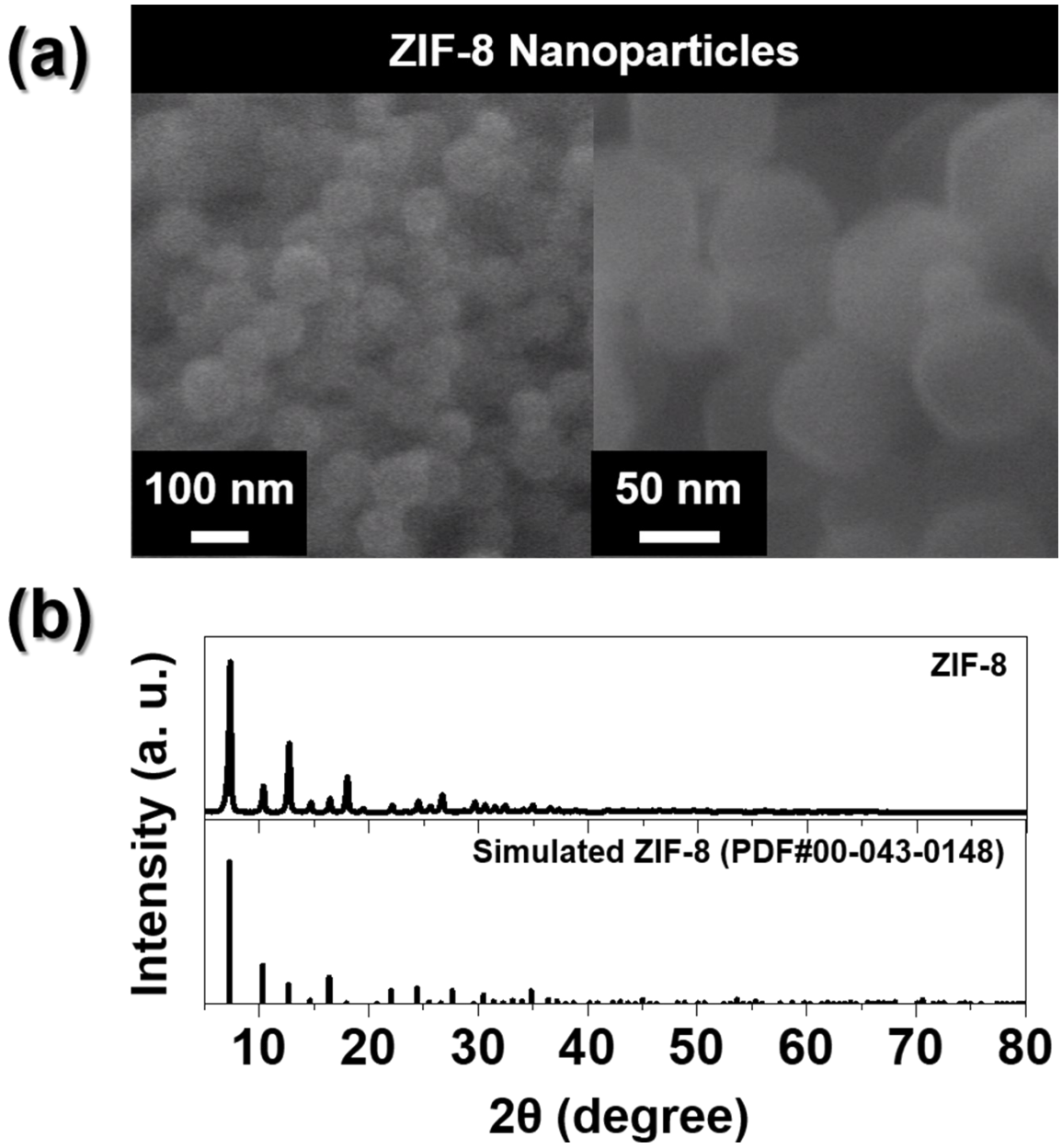

Fig. S1. (a) SEM images and (b) XRD pattern of ZIF-8 nanoparticles.

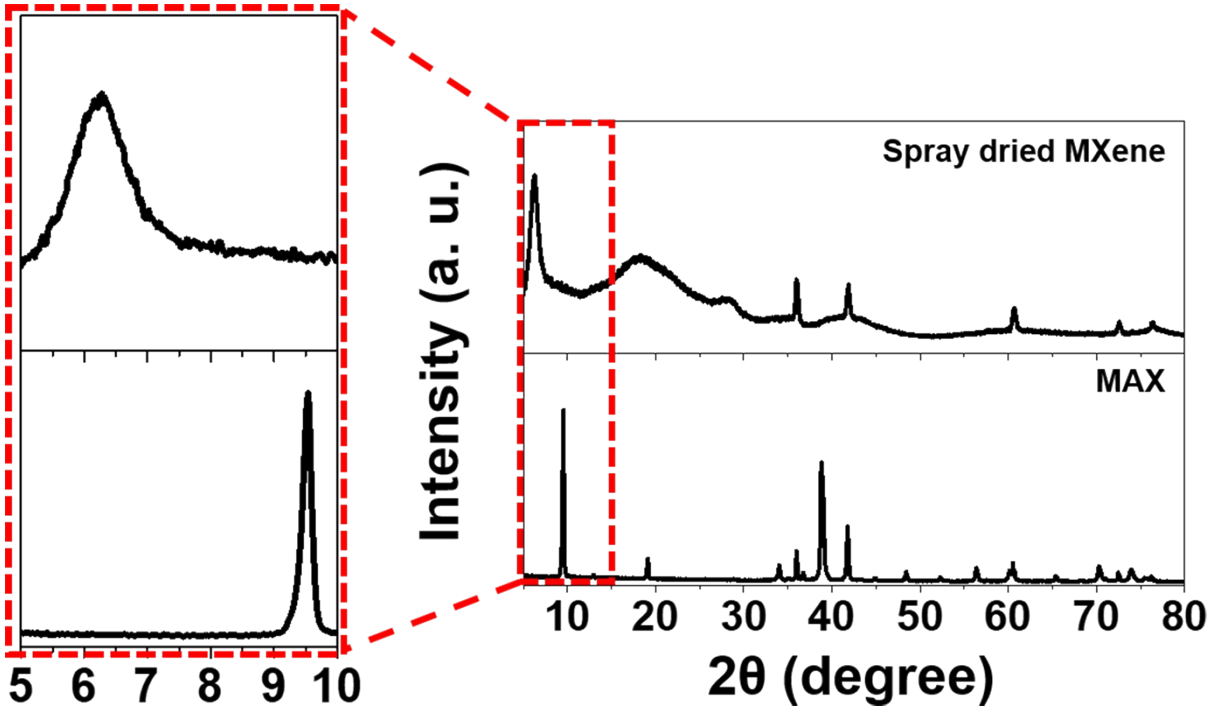

Fig. S2. XRD patterns of spray dried MXene and MAX.

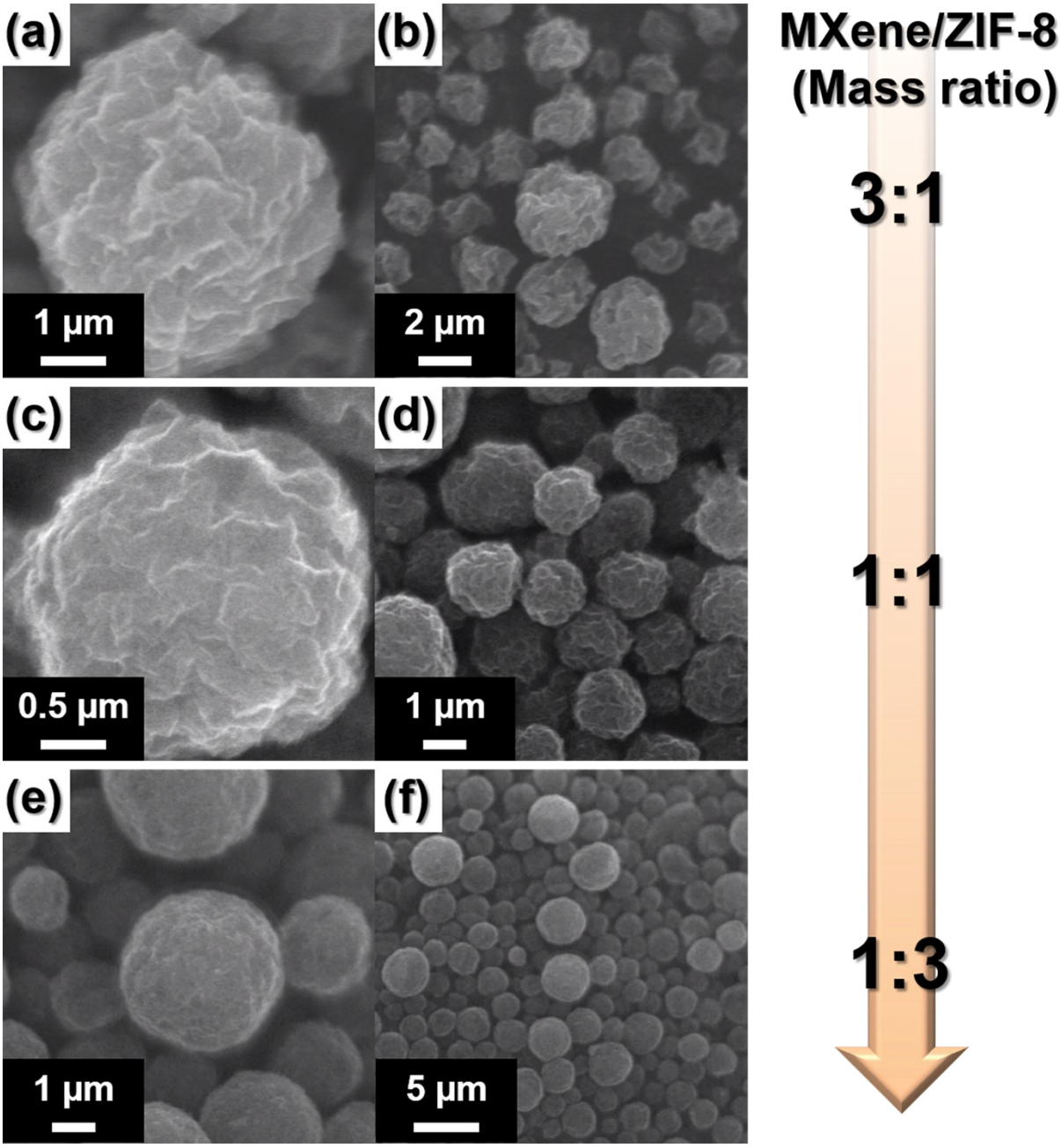

Fig. S3. SEM images of MXene/ZIF-8 with different mass ratios: (a and b) 3:1 (MXene:ZIF-8), (c and d) 1:1, and (e and f) 1:3.

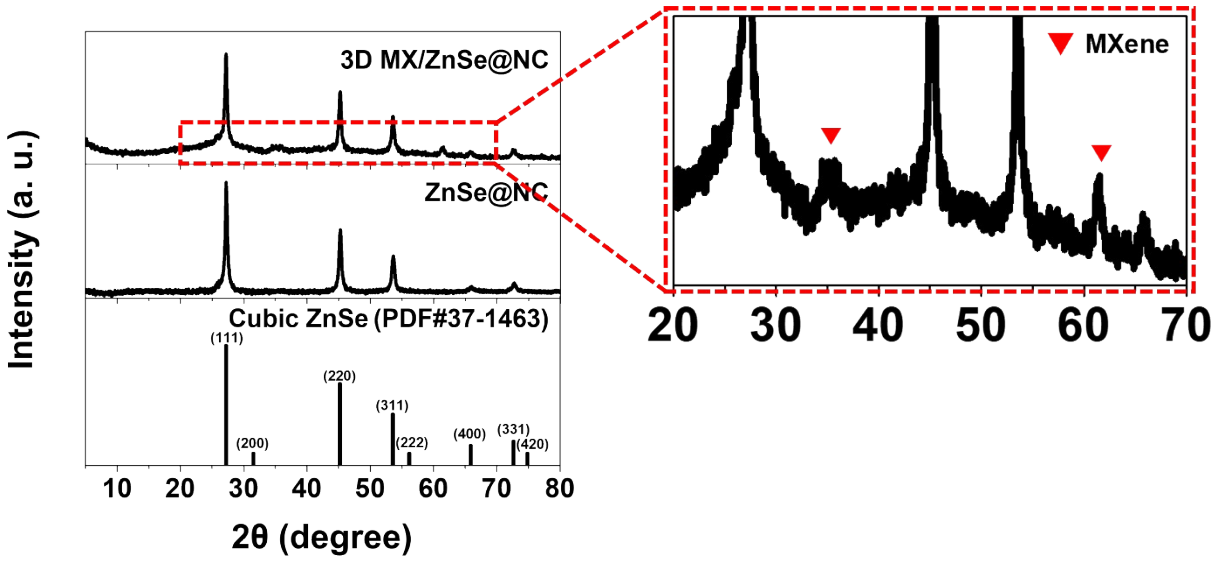

Fig. S4. XRD patterns of 3D MX/ZnSe@NC and ZnSe@NC.

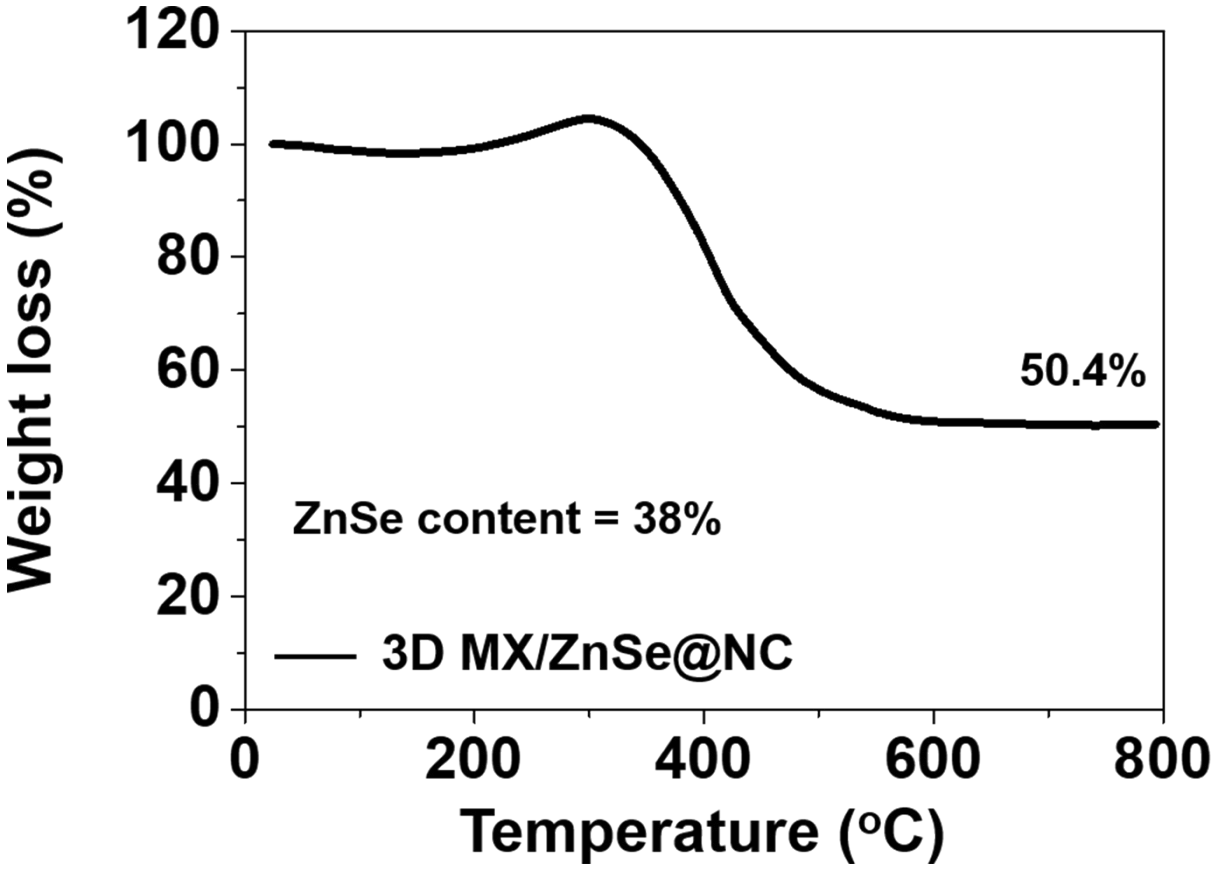

Fig. S5. TGA curve of 3D MX/ZnSe@NC.

Based on the TGA curve, the content of ZnSe in ZnSe@MXene could be calculated as follows, assuming that only ZnO and TiO_2 remain after 800 ℃. Considering the moisture evaporation, the residual ZnO and TiO_2 content is 51.2 %.

The MX/ZIF-8 microsphere prepared by the spray drying process underwent two post-treatment; carbonization and selenization. After each process, the huge weight change of the sample was confirmed; 1) carbonization (- 39.6 %) and 2) selenization (+ 32.6 %). Considering the MXene content of pristine MX/ZIF-8 is 25 % (= 25 g of MXene in 100 g of MX/ZIF-8), the MXene content of MX/ZnSe@NC could be calculated to be 31 %.

To determine the weight ratio of ZnSe in MX/ZnSe@NC, it was assumed that the total weight of MX/ZnSe@NC was 100 g. Before TGA, the contents of MXene, PVP-derived carbon, and ZnSe are 31 g, A g, and (69-A) g, respectively. After TGA, the MXene was transformed to TiO_2

with a weight decrease of 4 % according to a previous study [1], while the ZnSe was transformed to ZnO and the weight is $\frac{(69 - A) \times 81.4}{144.4} g$ (refer to the equation below).

$$(69 - A)\, g\, ZnSe \times \frac{1\, mol\, ZnSe}{144.4 g\, ZnSe} \times \frac{1\, mol\, ZnO}{1\, mol\, ZnSe} \times \frac{81.4 g\, ZnO}{1\, mol\, ZnO} = \frac{(69 - A) \times 81.4}{144.4} g$$

From the TG curve, the total content of ZnO and TiO_2 is 51.2 % (= 51.2 g) **therefore the weight of ZnSe can be determined to be 38 g.**

	ZnSe (g)	**C (g)**	**MXene (g)**	**Total (g)**
Before TGA	69-A	A	31	100
		-100 %	-4 %	
After TGA	$\frac{(69 - A) \times 81.4}{144.4}$	0	29.76	51.2

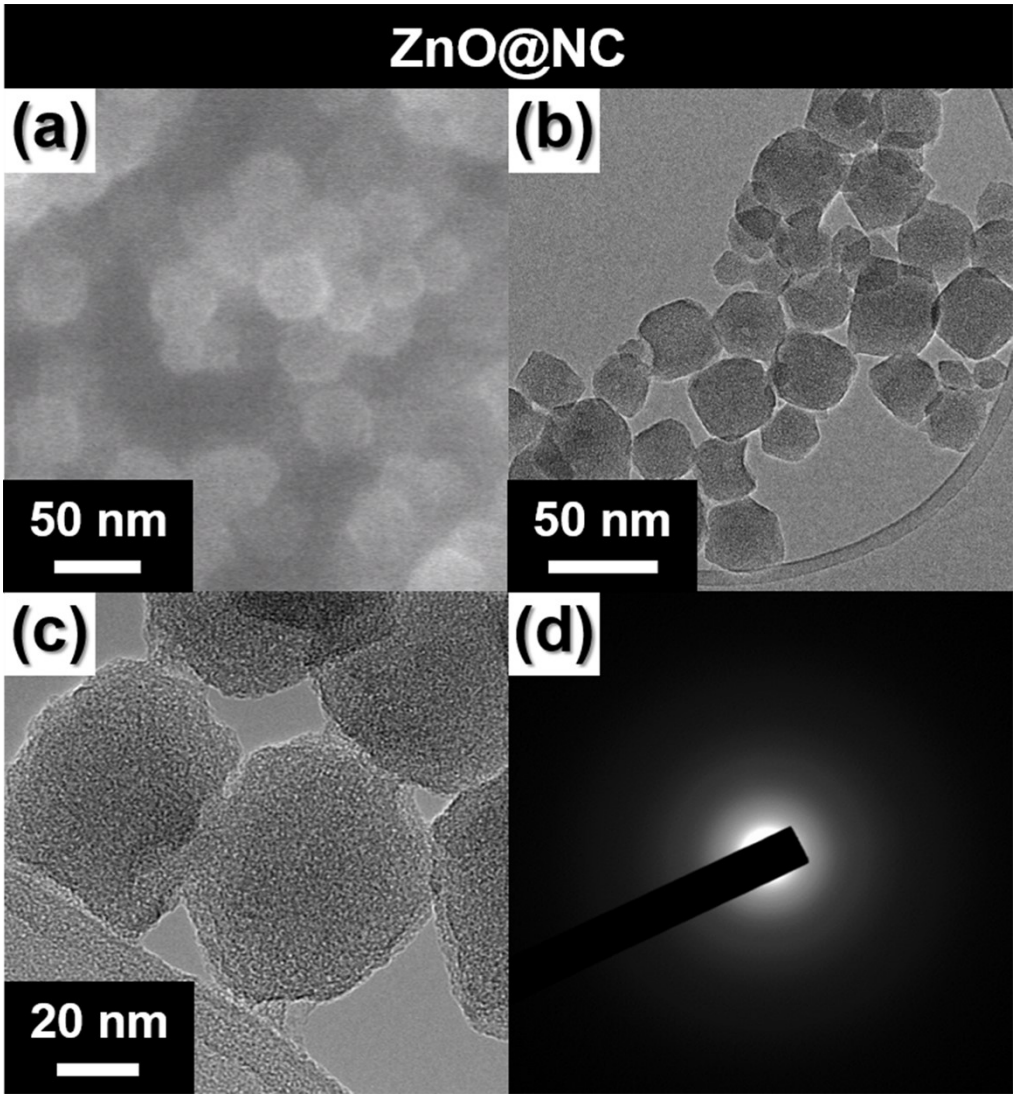

Fig. S6. (a) SEM image, (b and c) TEM images, and (d) SAED pattern of ZnO@NC.

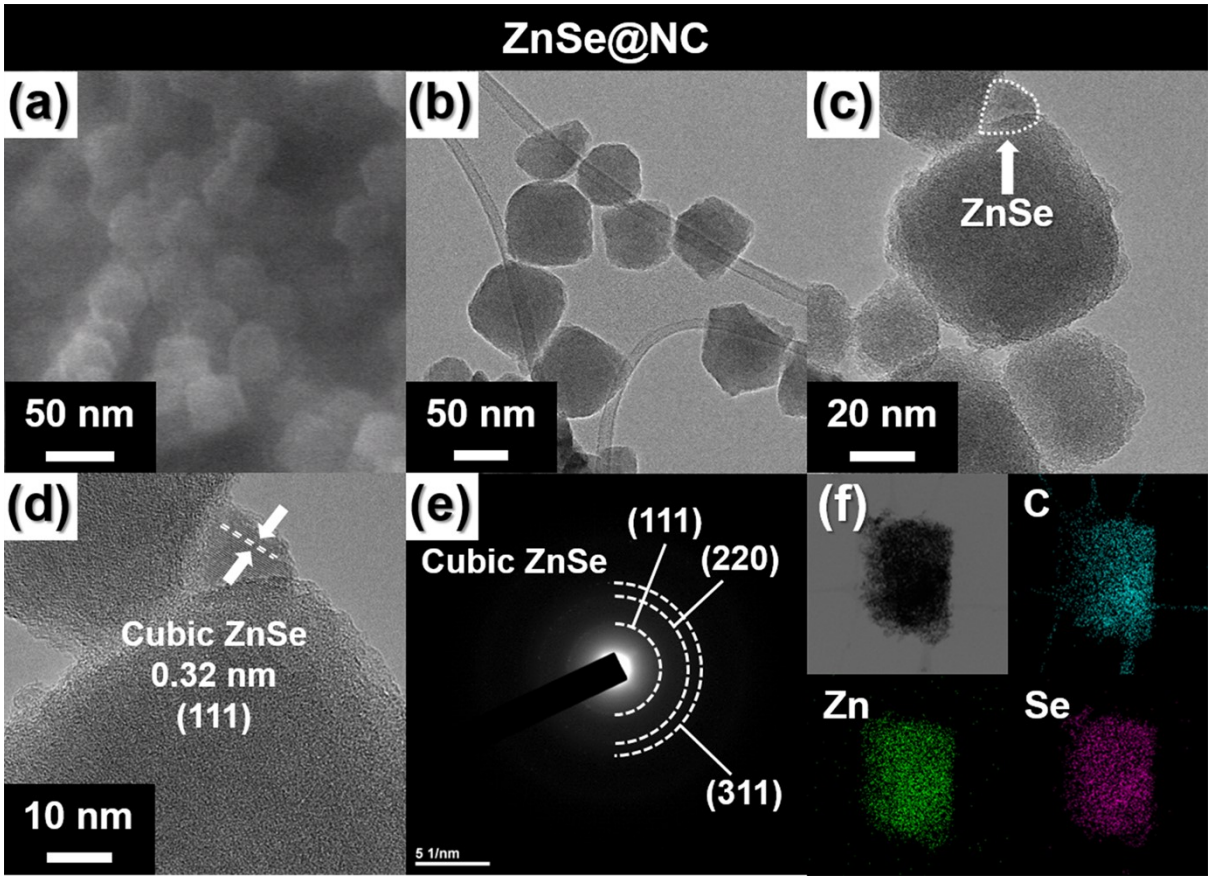

Fig. S7. (a) SEM image, (b and c) TEM images, (d) HR-TEM image, (e) SAED pattern, and (f) elemental mapping of ZnSe@NC.

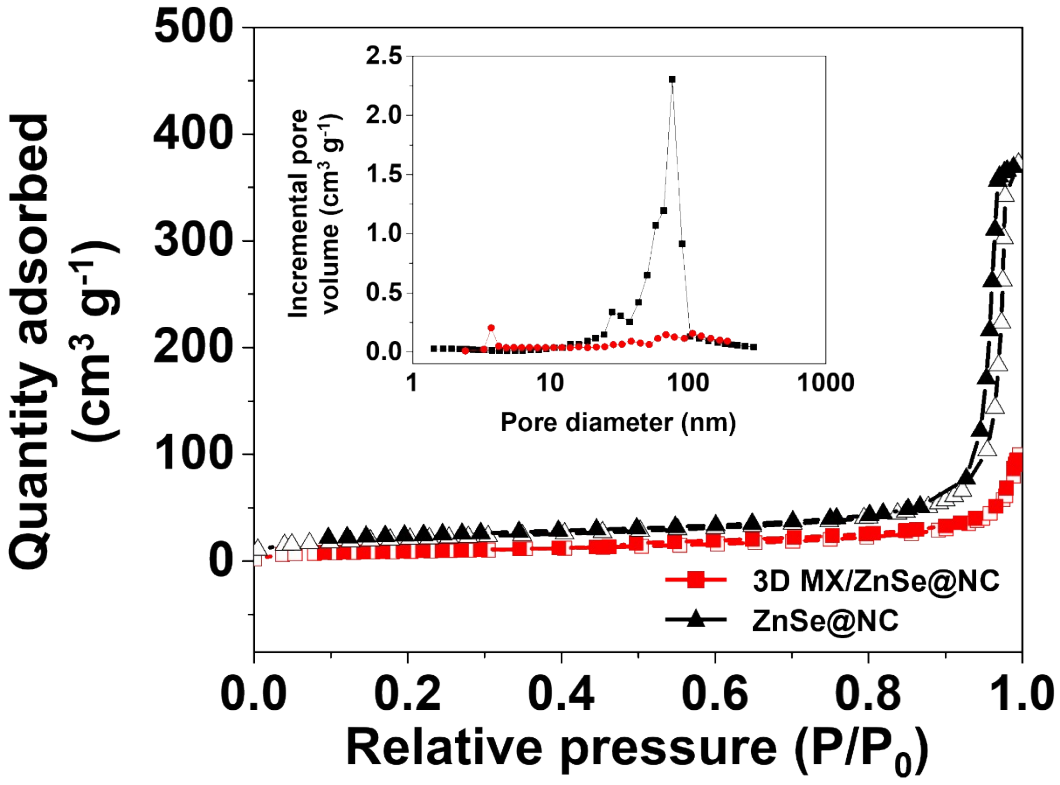

Fig. S8. N_2 adsorption/desorption isotherms and BJH pore size distributions of 3D MX/ZnSe@NC and ZnSe@NC.

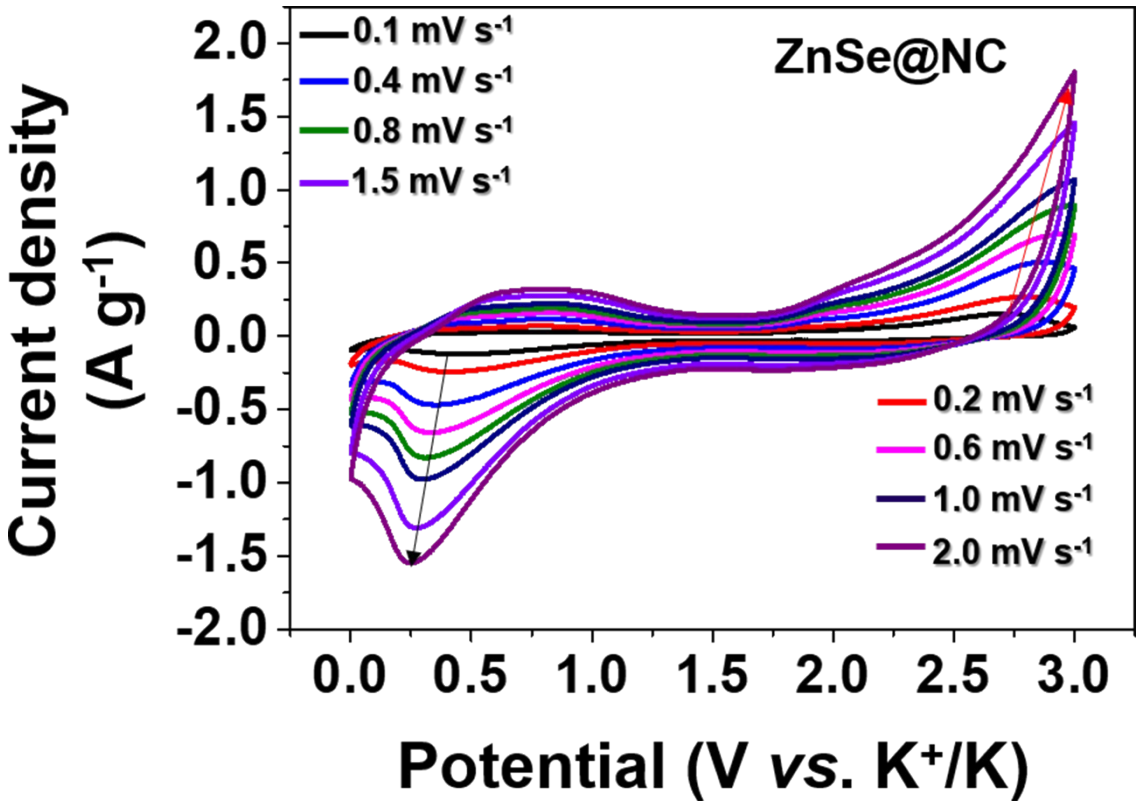

Fig. S9. CV curves of ZnSe@NC obtained at different scan rates.

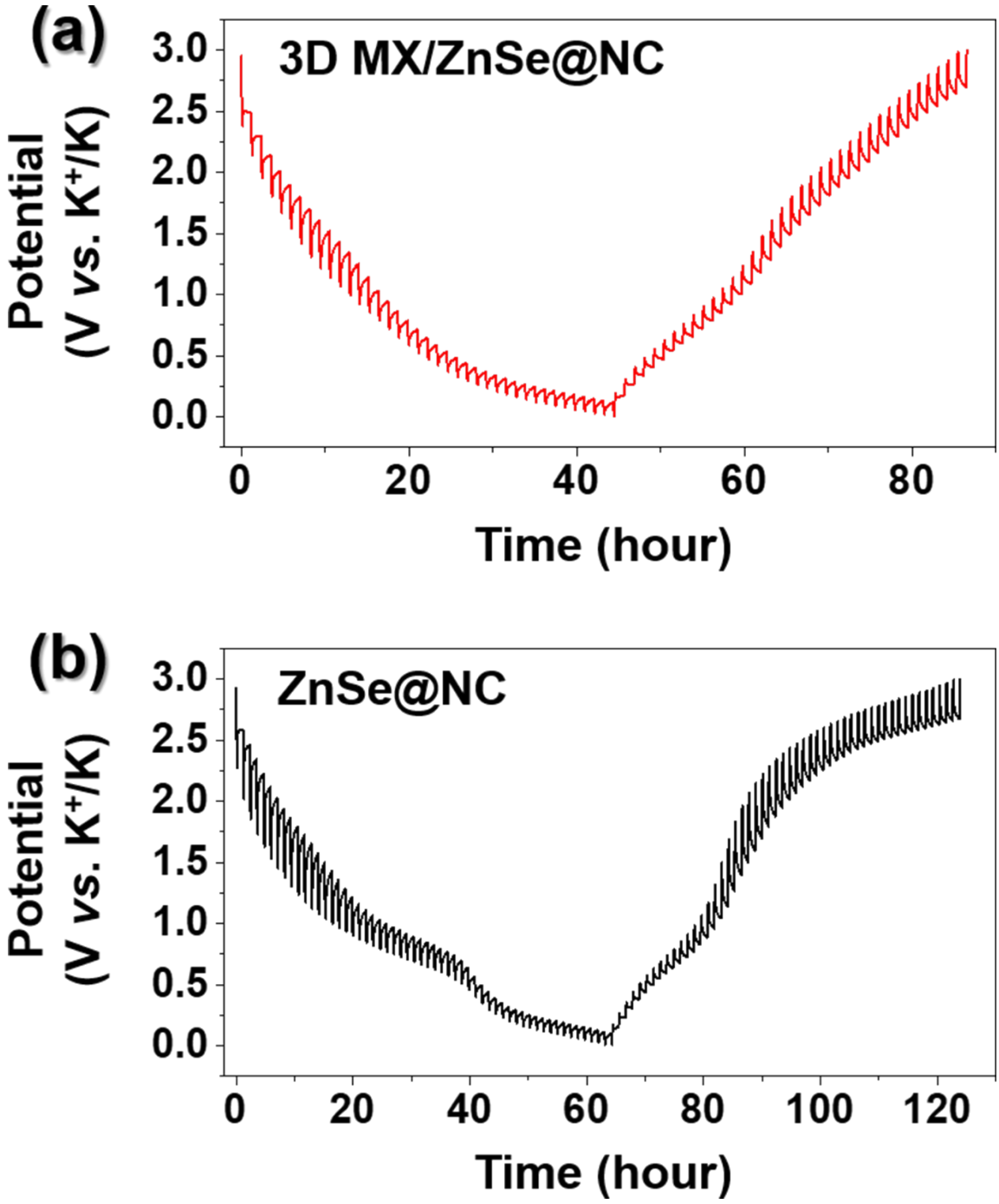

Fig. S10. GITT profiles of (a) 3D/MX@ZnSe@NC and (b) ZnSe@NC electrodes

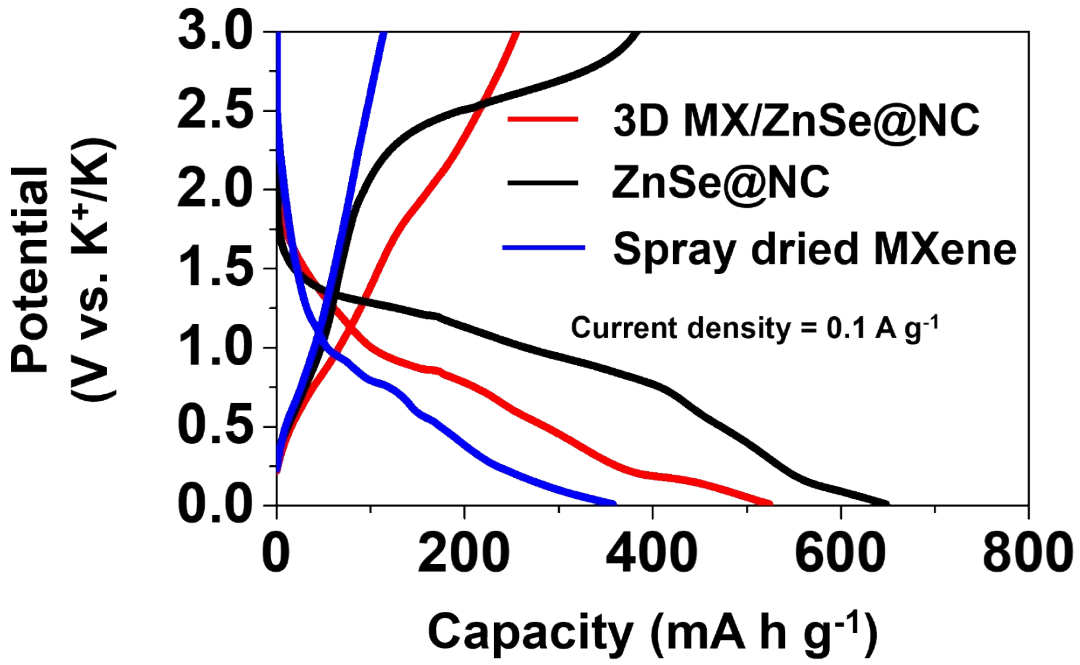

Fig. S11. Galvanostatic charge/discharge (GCD) profiles of 3D MX/ZnSe@NC, ZnSe@NC, and spray dried MXene electrodes tested at 0.1 A g^{-1}

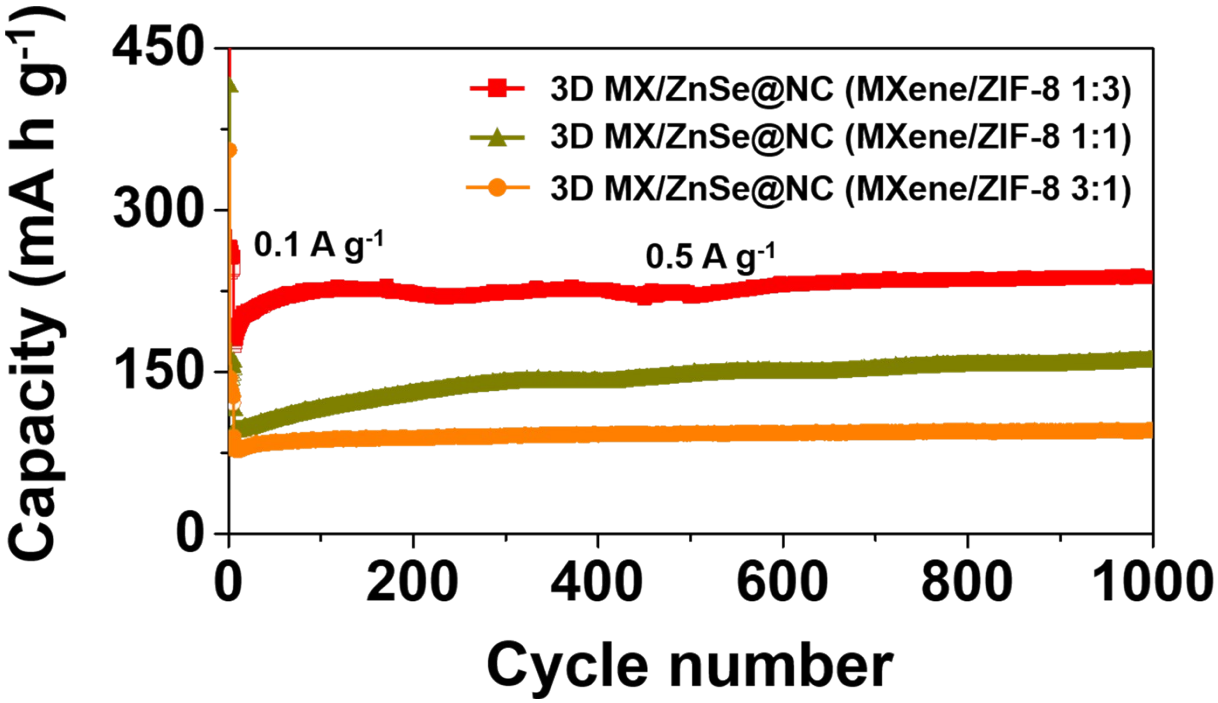

Fig. S12. Cycling performances of MX/ZnSe@NC with different mass ratios of MXene and ZIF-8.

Table. S1. Electrochemical properties of various Zn-based anode for PIBs reported in the previous studies.

Morphology	Synthesis method	Voltage window [V]	Current density [mA g^{-1}]	Discharge capacity [mA h g^{-1}] (Cycle)	Rate performance [mA h g^{-1}] (Current density)	Ref.
3D MX/ZnSe@NC	**Electrospinning**	**0.01-3**	**500**	**240 (1000th)**	**110 (2 A g^{-1})**	**our work**
ZnSe/C	hydrothermal	0.01-2.5	50	318 **(50th)**	205 (0.5 A g^{-1})	2
ZnSe@NC	hydrothermal	0.01-3	100	188.1 **(100th)**	122.5 (0.5 A g^{-1})	3
ZnS QDs-rGO	solvothermal	0.01-3	100	350.4 **(200th)**	98.8 (2 A g^{-1})	4
ZnSC@C@RGO	solvothermal	0.01-2.5	100	254 **(100th)**	162 (0.5 A g^{-1})	5
ZnSe@NPC	wet chemistry	0.01-3	100	264.3 **(200th)**	52.8 (5 A g^{-1})	6
d-ZnSe@HC	hydrothermal	0.01-3	100	400 **(100th)**	240 (3 A g^{-1})	7
ZnSe NP@NHC	Solvent thermal	0.3-2.9	25	237.4 **(100th)**	-	8
MP-ZnSe@NC NB	hydrothermal	0.01-3	500	247 **(500th)**	100 (3 A g^{-1})	9

Table. S2. Fitted values of EIS data in different states.

Sample	Fresh		1st			20th			100th		
	R_S	R_{CT}	R_S	R_{SEI}	R_{CT}	R_S	R_{SEI}	R_{CT}	R_S	R_{SEI}	R_{CT}
3D MX/ZnSe@NC	5.17	12468	5.26	38.7	5532	4.81	42	1125	4.63	34.6	577
ZnSe@NC	5.73	11086	5.73	61	4108	4.72	75.8	1853	4.21	45	914

Reference

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