

## Supporting Information

### **Multifunctional protective layer filled with 2D anionic nanosheets enabling dendrite-free zinc anode**

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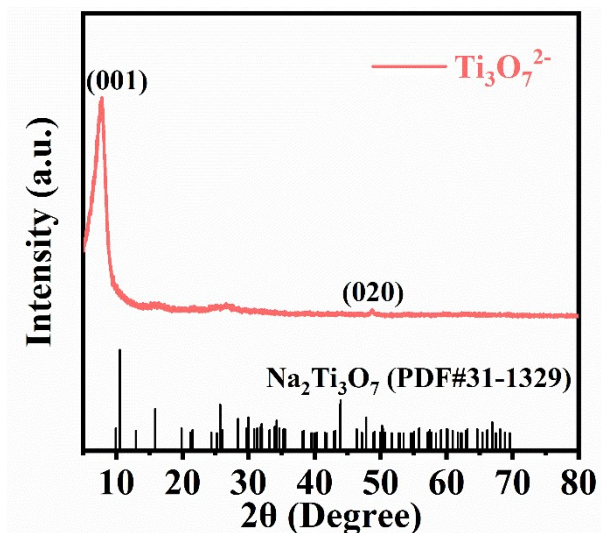


Fig. S1 XRD pattern of  $\text{Ti}_3\text{O}_7^{2-}$  nanosheets.

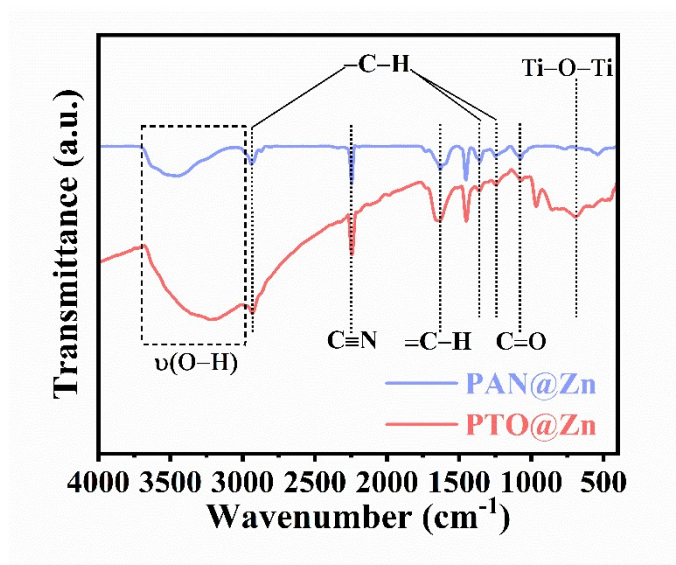


Fig. S2 FTIR spectrum of PAN@Zn and PTO@Zn.

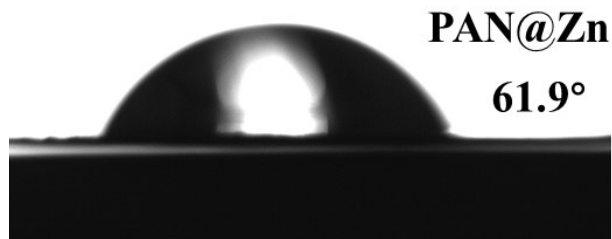


Fig. S3 Contact angles of PAN@Zn electrode.

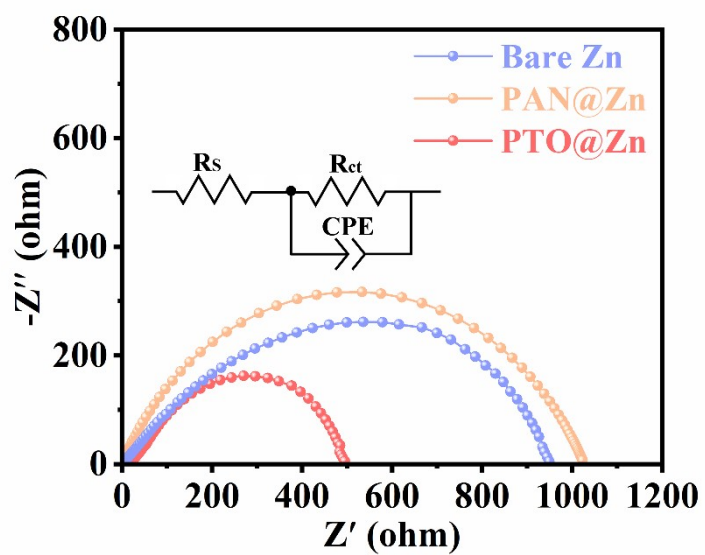
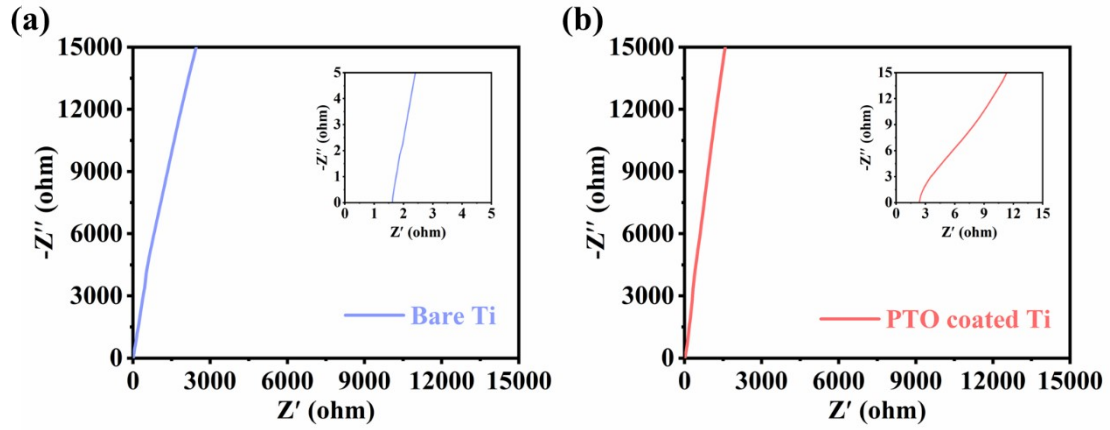


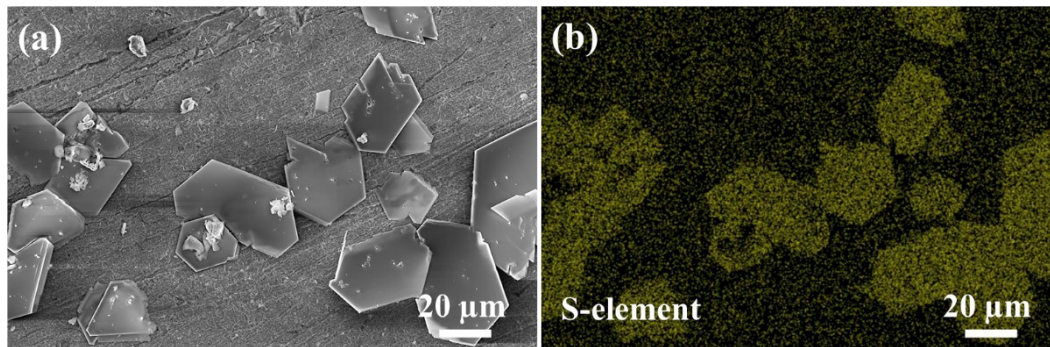
Fig. S4 EIS spectra of the bare Zn, PAN@Zn and PTO@Zn symmetric cells.



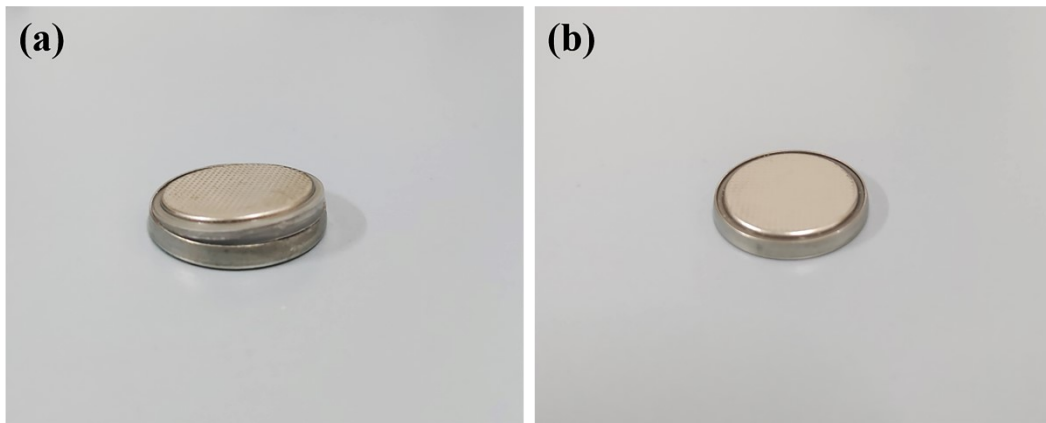
**Fig. S5** Nyquist plots over the frequency range of 100 kHz to 10 mHz of (a) the symmetrical cell with Ti as electrodes and (b) the symmetrical cell with PTO-coated Ti as electrodes (inset: enlargement of indicated range). The ionic conductivity ( $\sigma$ ) is calculated according to the following equation,

$$\sigma = \frac{L}{R_b \cdot S}$$

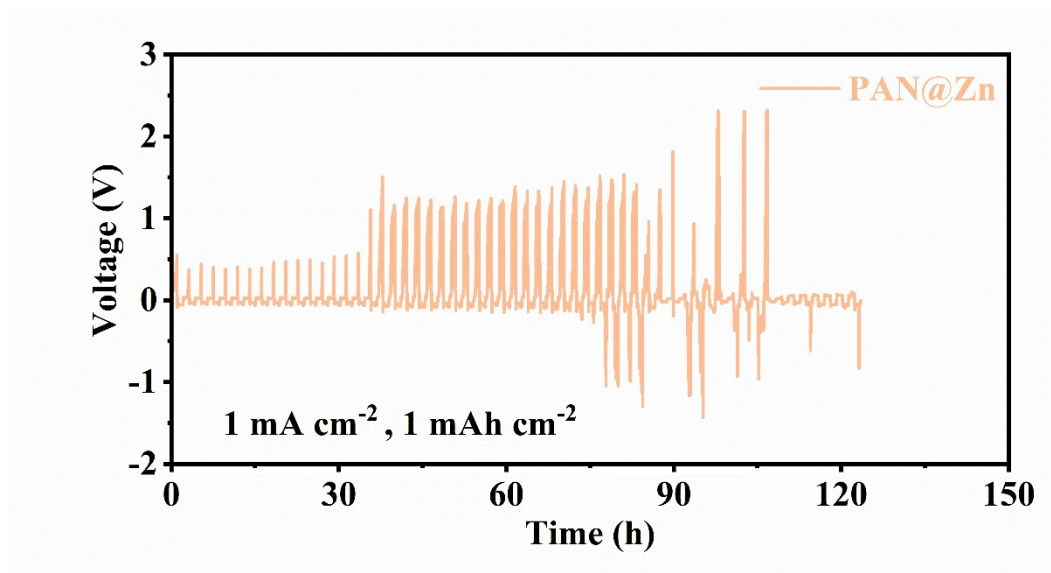
where L is the thickness of the PTO layer,  $R_b$  is the bulk impedance of the PTO layer, and S is the contact area.



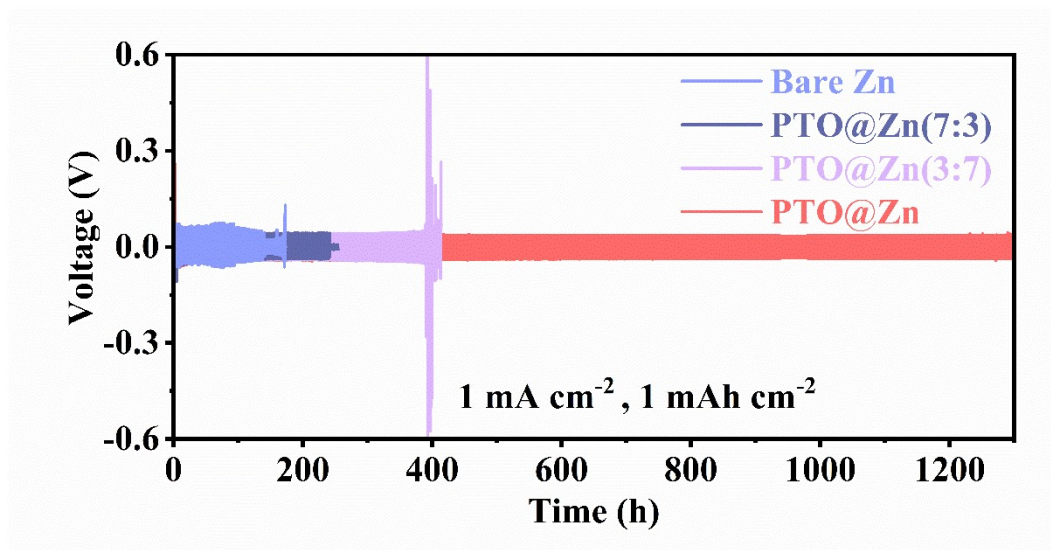
**Fig. S6** (a) SEM image and (b) corresponding EDS mapping of S element of the Zn foil after being soaked in 2 M  $ZnSO_4$  for 10 days.



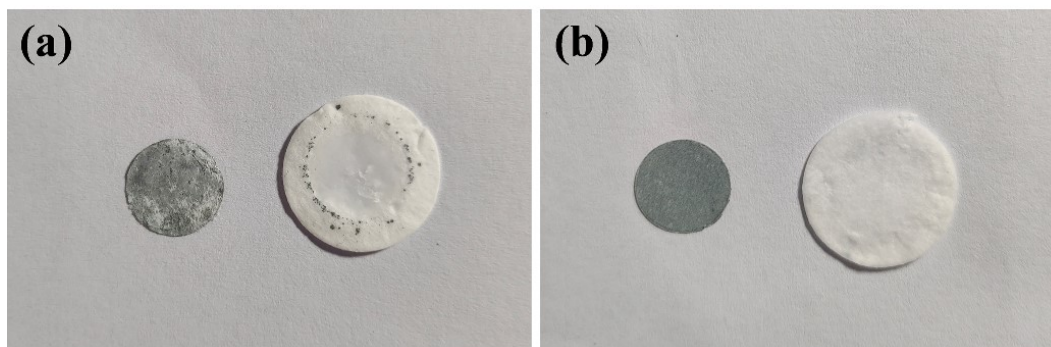
**Fig. S7** Photographs of (a) bare Zn and (b) PTO@Zn symmetrical battery after stripping/plating.



**Fig. S8** Cycling performance of symmetrical PAN@Zn||PAN@Zn cell at 1 mA cm<sup>-2</sup> with a capacity of 1 mAh cm<sup>-2</sup>.



**Fig. S9** Cycling performance of symmetrical Zn||Zn and PTO@Zn||PTO@Zn cells at  $1 \text{ mA cm}^{-2}$  with a capacity of  $1 \text{ mAh cm}^{-2}$ . The PTO coating layers have different mass ratios of PTO and 2D  $\text{Ti}_3\text{O}_7^{2-}$  nanosheets. For the layers with  $m(\text{PAN}):m(\text{Ti}_3\text{O}_7^{2-})$  ratios of 1:1, 7:3 and 3:7, the electrodes are denoted as PTO@Zn, PTO@Zn(7:3), and PTO@Zn(3:7), respectively.



**Fig. S10** Digital images of the electrodes and separators disassembled from the (a) bare Zn and (b) PTO@Zn symmetric cells after 20 cycles at  $5 \text{ mA cm}^{-2}/5 \text{ mAh cm}^{-2}$ .



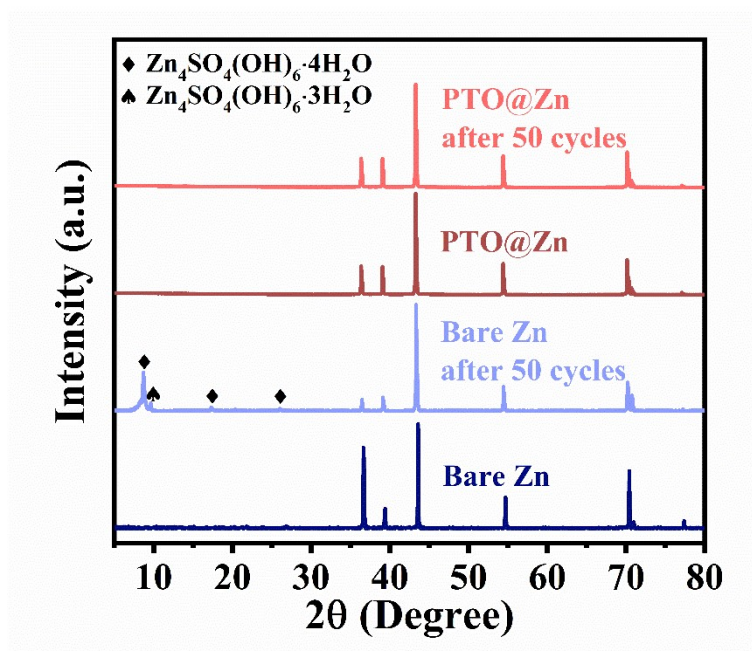


Fig. S11 The XRD patterns of the bare Zn and PTO@Zn before and after cycling.

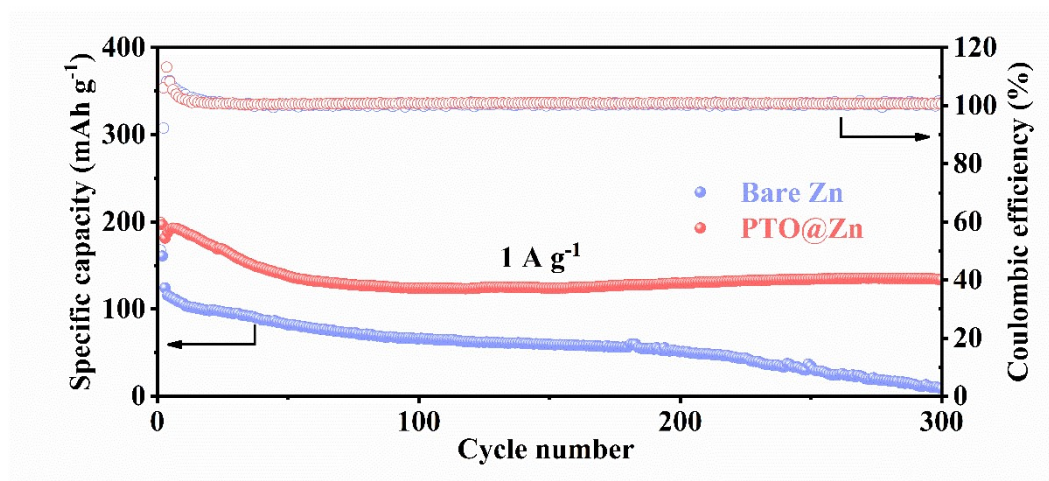


Fig. S12 Cycling performance of Zn|| $\text{MnO}_2$  and PTO@Zn|| $\text{MnO}_2$  cells under low N/P ratio cycled at  $1 \text{ A g}^{-1}$ .

**Table S1.** Comparison of cycling performance for this work with recently reported Zn-based Zn||MnO<sub>2</sub> full cells.

Anode (Thickness, $\mu\text{m}$ )	Cathode mass loading ( $\text{mg cm}^{-2}$ )	N/P ratio	Current density	Specific capacity ( $\text{mAh g}^{-1}$ )	Reference
Zn <sub>0.73</sub> Al <sub>0.27</sub> @Zn (200)	2.0	~63	1.2 C (1C = 616 mA g <sup>-1</sup> )	~243	1
Zn Sn (20)	1.2	~33	1 A g <sup>-1</sup>	124	2
Zn Sn (250)	15.8	~31	0.2 A g <sup>-1</sup>	92	
Zn@MCFs (100)	1.0	/	1 A g <sup>-1</sup>	236.1	3
AEC-Zn (80)	1.0	/	2 C (1 C=308 mA g <sup>-1</sup> )	244	4
Cu@Zn (40)	1.5	/	1 A g <sup>-1</sup>	~120	5
PA-Zn (20)	~1.3	/	2 C (1 C=300 mA g <sup>-1</sup> )	176.1	6
	~15	/		175	
ZnS@Zn (10)	~0.8	/	5 C (1 C=308 mA g <sup>-1</sup> )	125.8	7
Zn-VSGDY (10)	1.3-2.6	/	1 A g <sup>-1</sup>	125.4	8
PTO@Zn (30)	1.0-1.2	~47	1 A g <sup>-1</sup>	198.6	This work
PTO@Zn (10)	~2.1	~9		196.8	



## Reference

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