

Supporting Information

Reversible Zn²⁺/Al³⁺ intercalation in niobium-substituted polyoxometalates and demonstration of energy storage smart window

Tong Feng ^{a,b}, Huili Guo ^a, Xiaoxiao Xing ^a, Yan Bai ^{a,*}, Dongbin Dang ^{a,*}, Weizhen Zhao ^{b,*}

^a Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

^b Beijing Key Laboratory of Ionic Liquids Clean Process, CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

* Corresponding author: E-mail address: baiyan@henu.edu.cn (Y. Bai), dangdb@henu.edu.cn (D.-B. Dang), wzzhao@ipe.ac.cn (W.-Z. Zhao).

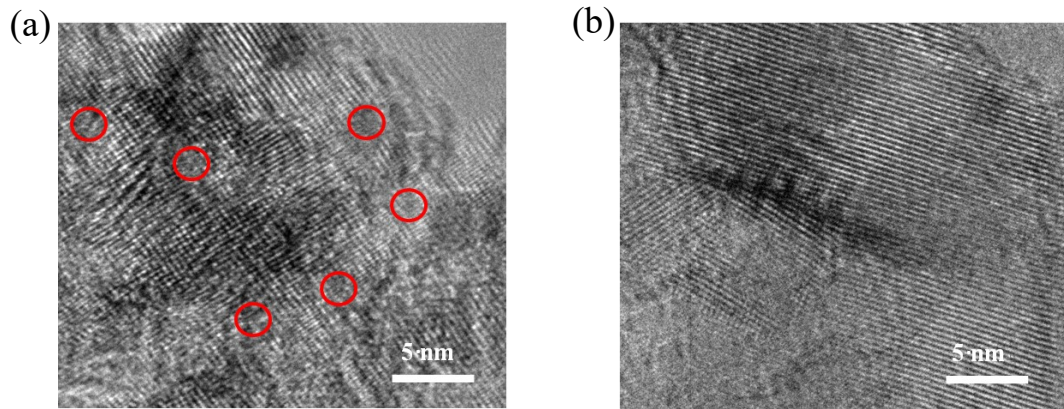


Fig. S1 Transmission electron microscopy (TEM) image of (a) $P_2W_{15}Nb_3$ - TiO_2 composite film and (b) TiO_2 film.

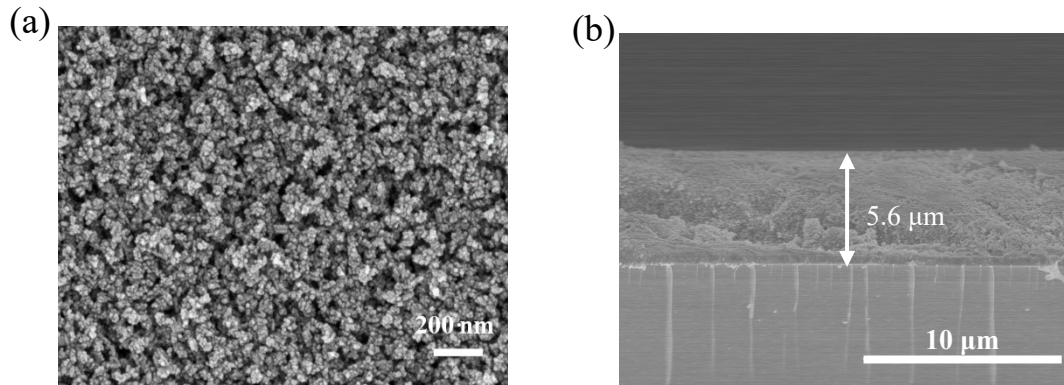


Fig. S2 (a) Top-view SEM images of TiO_2 film. (b) Cross-sectional SEM image of $P_2W_{15}Nb_3$ - TiO_2 composite film.

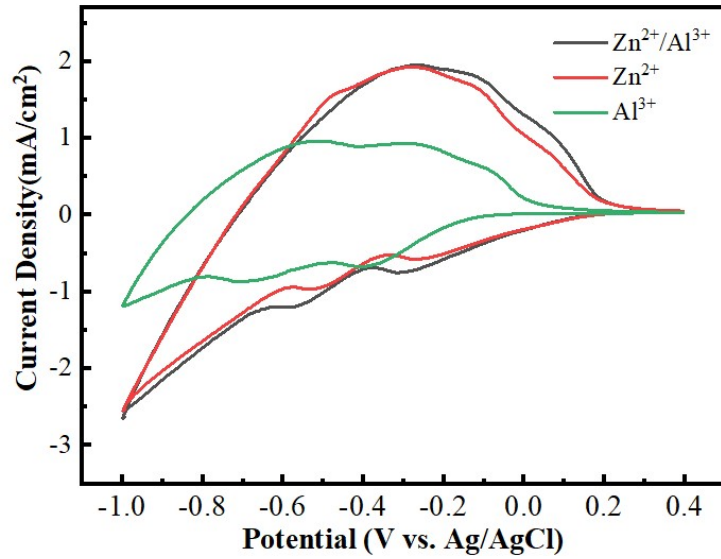


Fig. S3 CV curves of the $P_2W_{15}Nb_3-TiO_2$ composite film in 1 M $Zn(ClO_4)_2-Al(ClO_4)_3$, $Zn(ClO_4)_2$, $Al(ClO_4)_3$.

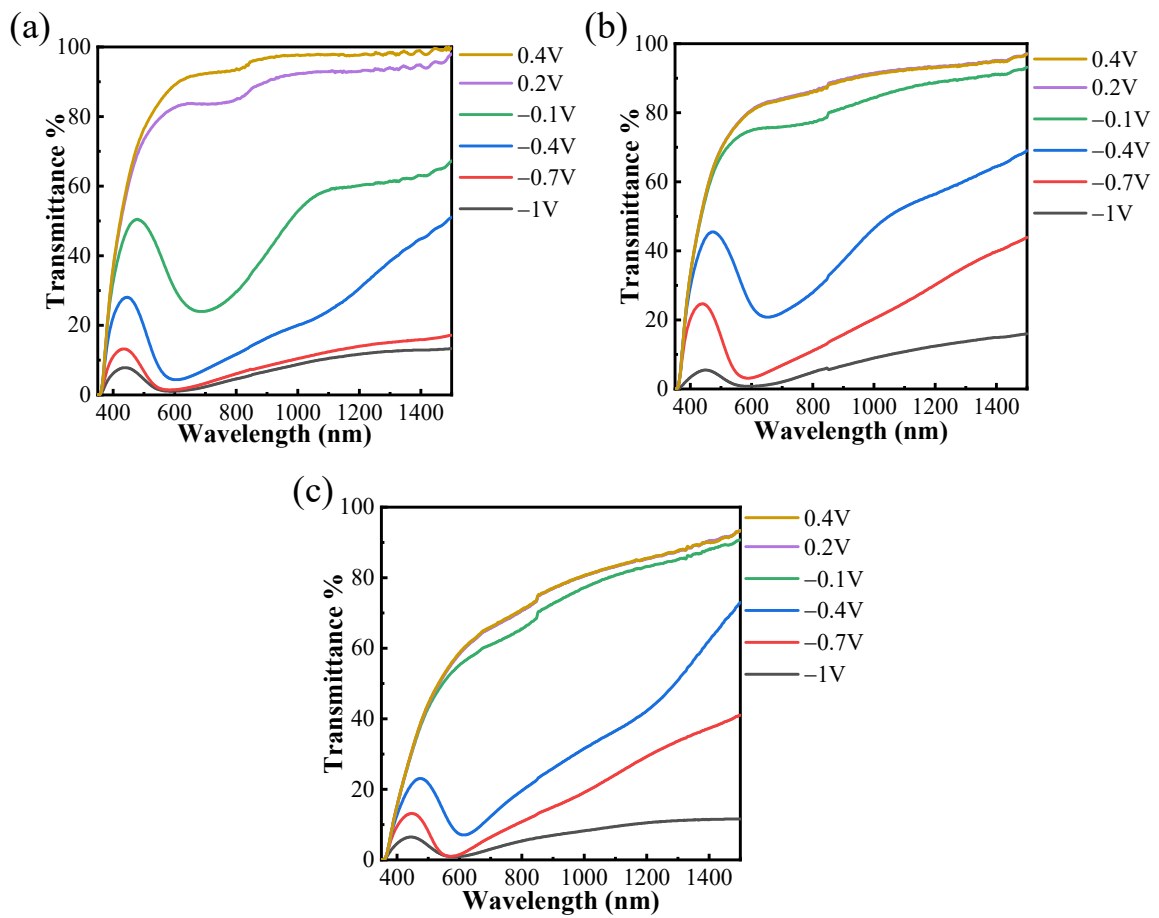


Fig. S4 Visible near-infrared transmittance spectra of $P_2W_{15}Nb_3-TiO_2$ composite film measured from -1 to 0.4 V in (a) 1 M $Zn(ClO_4)_2-Al(ClO_4)_3$, (b) $Zn(ClO_4)_2$, (c) $Al(ClO_4)_3$, respectively.

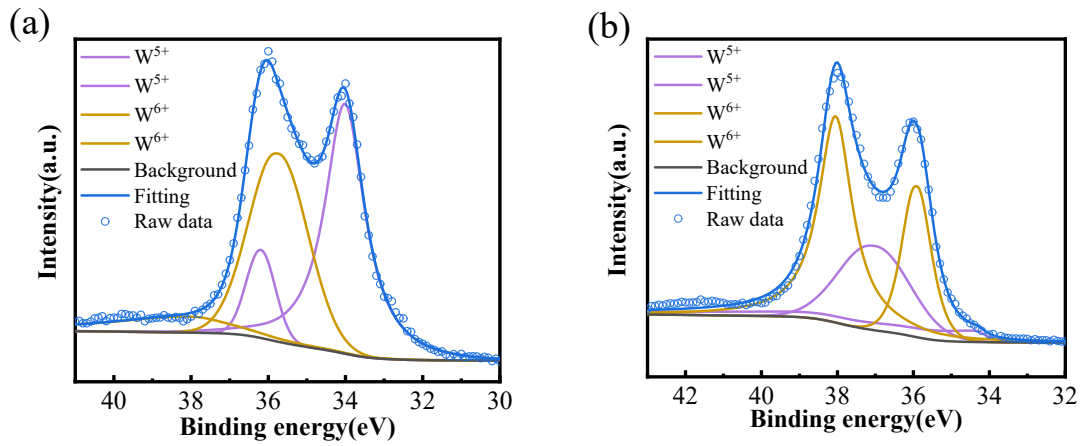


Fig. S5 W 4f XPS spectra of self-colored $P_2W_{15}Nb_3-TiO_2$ composite film in 1 M (a) $Zn(ClO_4)_2$, (b) $Al(ClO_4)_3$ electrolyte.

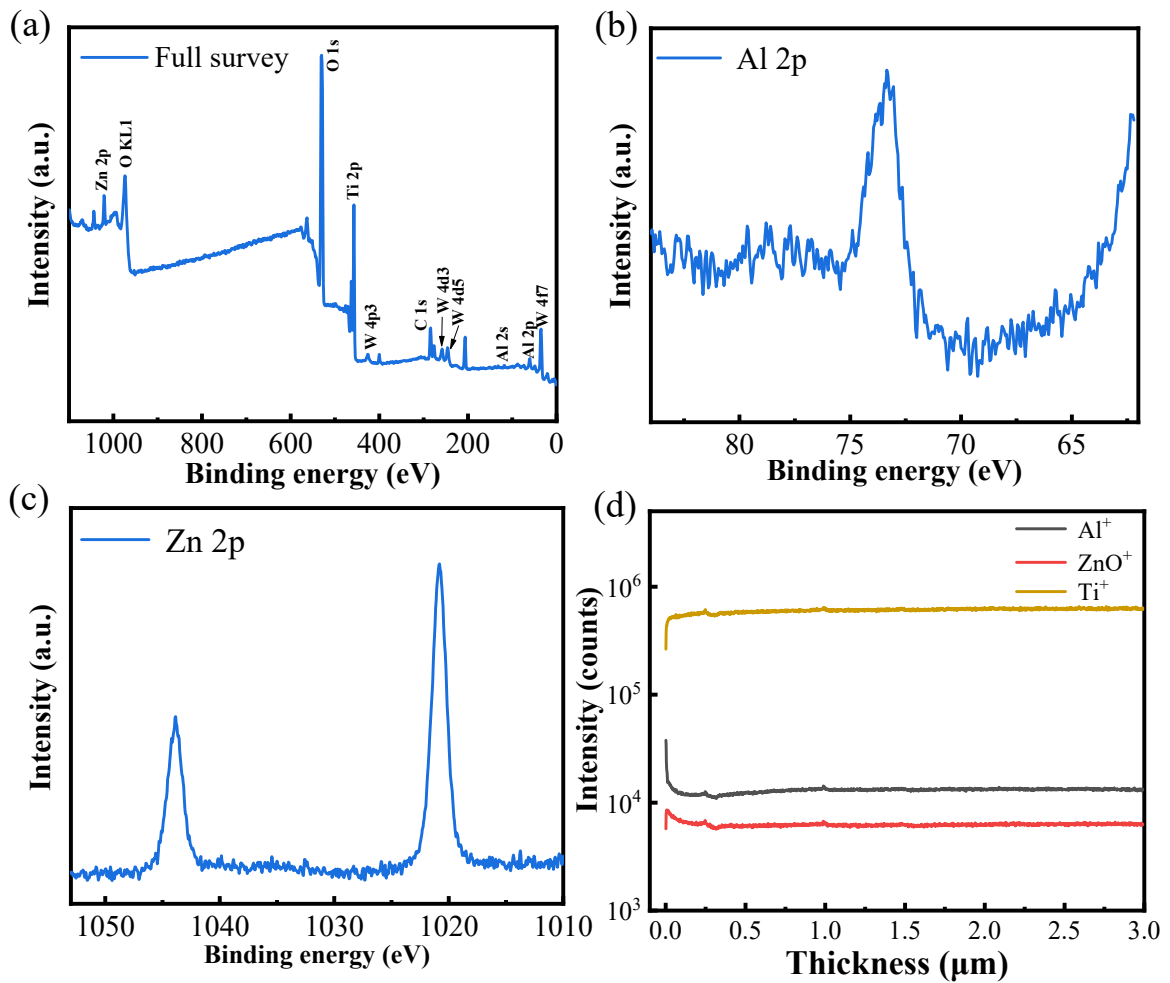


Fig. S6 (a) XPS full survey of $P_2W_{15}Nb_3-TiO_2$ composite film. (b) Al 2p and (c) Zn 2p XPS spectra of colored $P_2W_{15}Nb_3-TiO_2$ composite film in 1 M $Zn(ClO_4)_2-Al(ClO_4)_3$ electrolyte. (d) TOF-SIMS depth

profiles of $P_2W_{15}Nb_3-TiO_2$ composite film that measure at -1 V in 1 M $Zn(ClO_4)_2-Al(ClO_4)_3$ electrolyte.

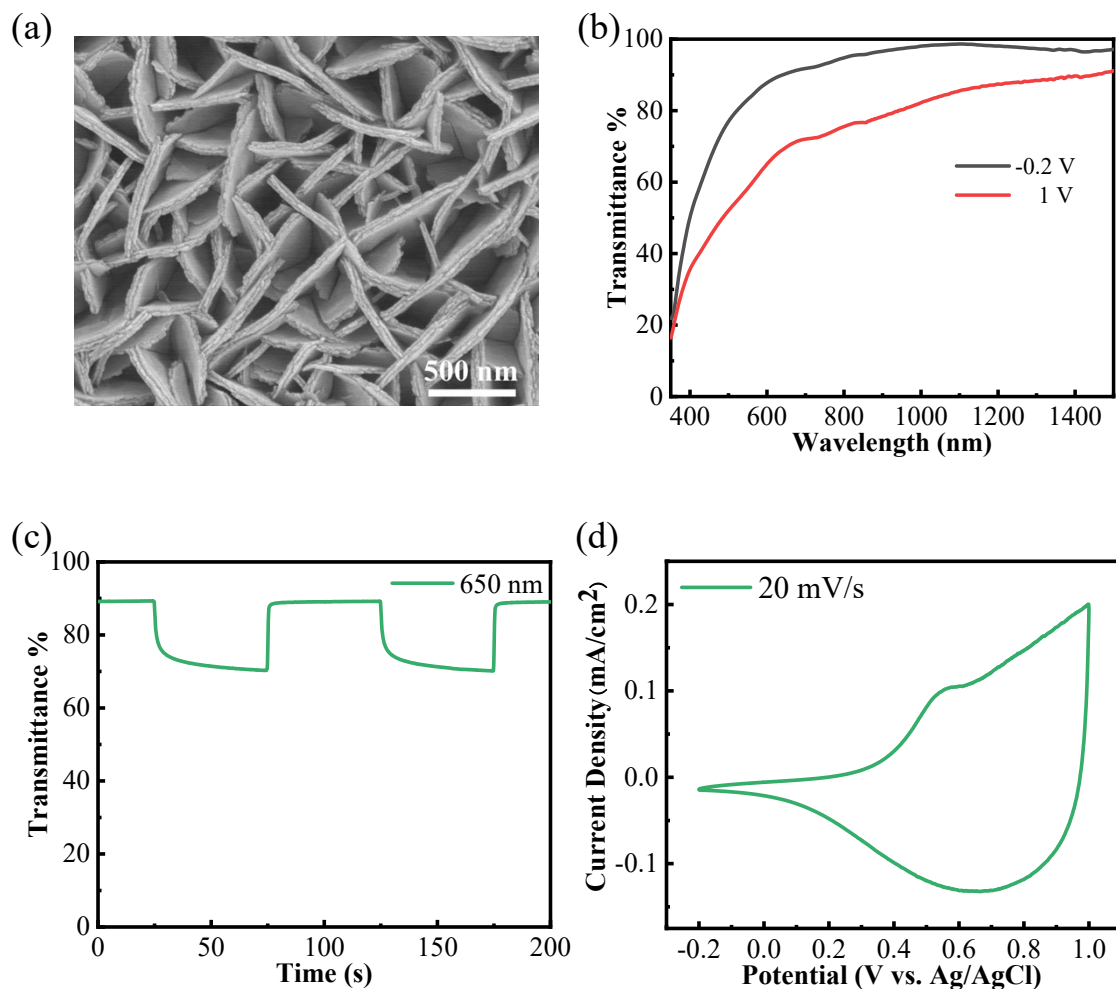


Fig. S7 (a) SEM image of NiO nanosheets. (b,c) Visible near-infrared transmittance spectra and dynamic optical transmittance measurements of the NiO film measured at -0.2 and 1 V in 1 M $Zn(ClO_4)_2-Al(ClO_4)_3$ electrolyte. (d) CV curves of the NiO film in 1 M $Zn(ClO_4)_2-Al(ClO_4)_3$ electrolyte.

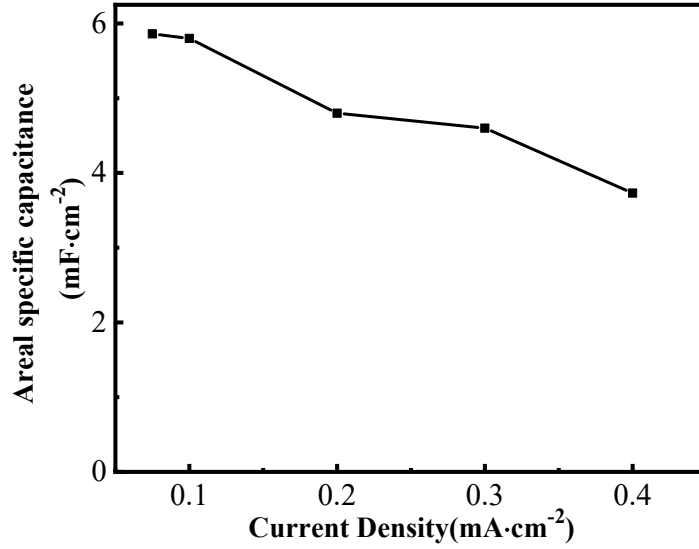


Fig. S8 Areal capacitances of EESD at different current densities.

Table S1 Comparison of Current State-of-the-Art Electrochromic Films and Devices

Materials	Film or Device	ΔT	Response Time T_b/T_c (s)	CE (cm ² C ⁻¹)	Areal Capability (mF cm ⁻²)	Spectral selectivity	Reference
P ₂ W ₁₅ Nb ₃ -TiO ₂	Film	~90% 650 nm	18/8	136	52	350-1500 nm	This work
	Device	~64% 650 nm	14/4	88	5.86		
Polyoxometalates-W ₁₈ O ₄₉	Film	~30% 500 nm	86/26	–	–	350-1400 nm	Gu et al ¹
WO _{3-x}	Film	~93% 633 nm	13/16	–	–	350-1800 nm	Zhang et al ²
	Device	~73% 650 nm	–	–	–		
NiO-PB	Film	~60% 630 nm	3.8/1.6	45.3	–	350-1000 nm	Pan et al ³
	Device	~67% 630 nm	7.9/2.8	109	11.5		
WO ₃	Device	~62% 650 nm	1.95/1.84	139	5.12	350-800 nm	Bi et al ⁴
PICA	Film	~43% 490 nm	0.7/1.7	142	16.2	350-1000 nm	Li et al ⁵
	Device	–	–	–	4.3		
NW-P ₂ W ₁₇ -Cu(phen) ₂	Film	~44% 490 nm	9.5/2.9	50.4	–	400-800 nm	Chu et al ⁶

Reference

1. H. Gu, C. Guo, S. Zhang, L. Bi, T. Li, T. Sun and S. Liu, *ACS Nano*, 2018, **12**, 559-567.
2. S. Zhang, S. Cao, T. Zhang, A. Fisher and J. Y. Lee, *Energy Environ. Sci.*, 2018, **11**, 2884-2892.
3. J. Pan, R. Zheng, Y. Wang, X. Ye, Z. Wan, C. Jia, X. Weng, J. Xie and L. Deng, *Sol. Energy Mater. Sol. Cells*, 2020, **207**, 110337.
4. Z. Bi, X. Li, Y. Chen, X. He, X. Xu and X. Gao, *ACS Appl Mater Interfaces*, 2017, **9**, 29872-29880.
5. J. Li, Q. Guo, Y. Lu and G. Nie, *European Polymer Journal*, 2019, **113**, 29-35.
6. D. Chu, X. Qu, S. Zhang, J. Zhang, Z. Liu, L. Zhou and Y. Yang, *Asia-Pac. J. Chem. Eng.*, 2022, **2779**, 1-9.