

Support information

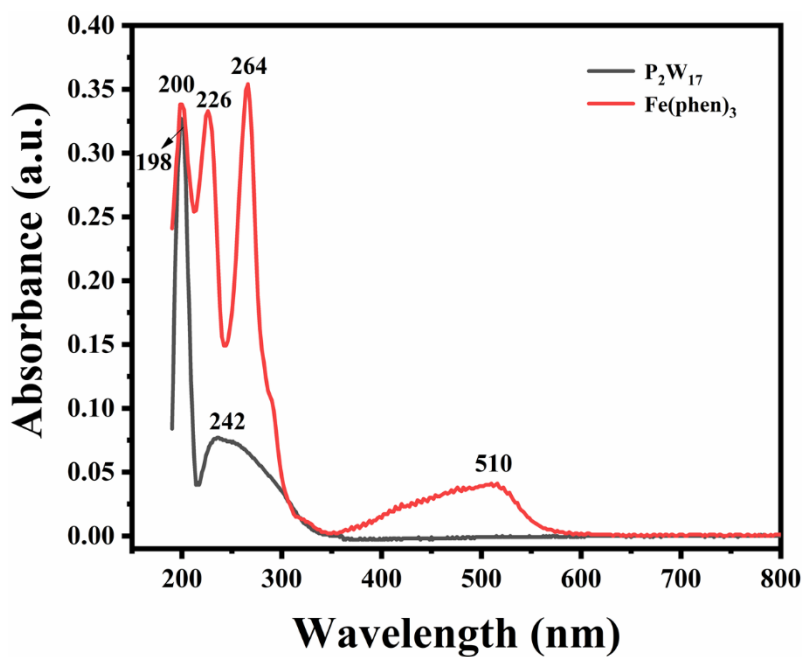


Fig. S1 UV-Vis absorption spectrum of P_2W_{17} and $Fe(phen)_3$.

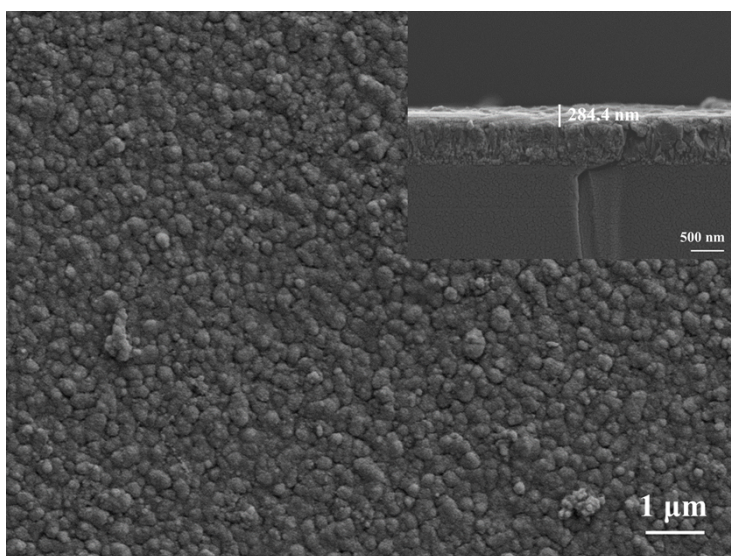


Fig. S2 Top-view SEM image of $P_2W_{17}/Fe(phen)_3$ composite film (inset: the cross-sectional view image)

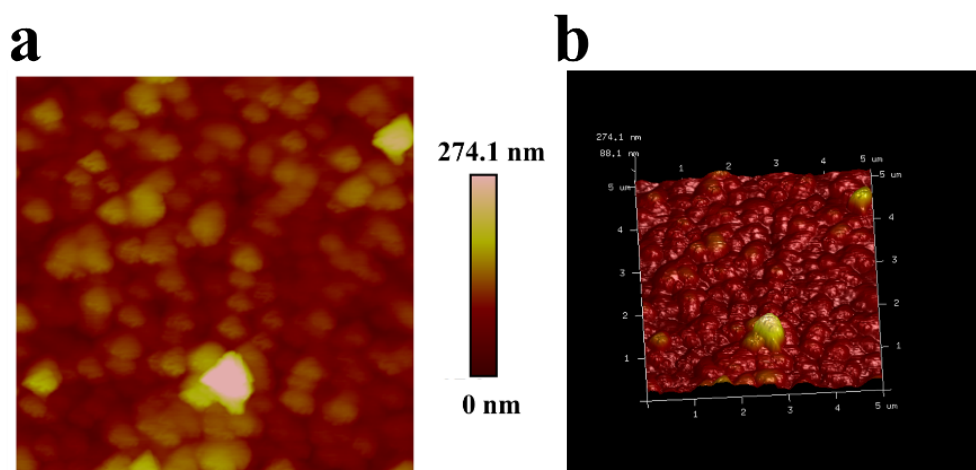


Fig. S3 (a) 2D and (b) 3D AFM images of $P_2W_{17}/Fe(phen)_3$ composite film.

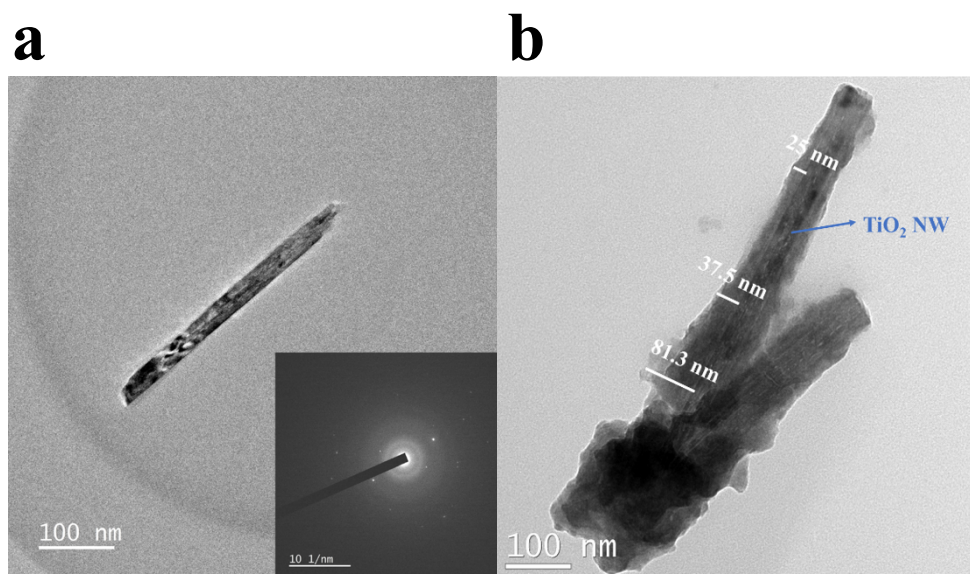


Fig. S4 The TEM image of (a) TiO_2 NW (inset image: The selected area electron diffraction pattern); (b) NW/ $P_2W_{17}/Fe(phen)_3$.

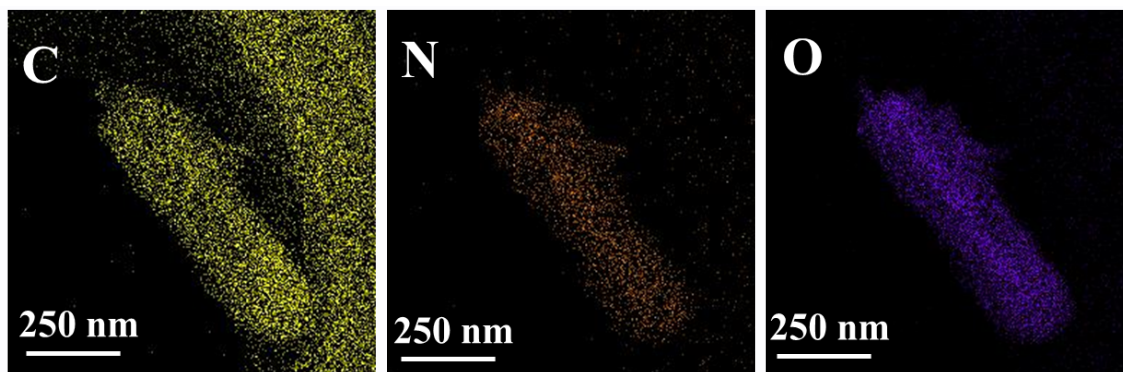


Fig. S5 EDS mapping images of NW/P₂W₁₇/Fe(phen)₃ for C, N, and O respectively.

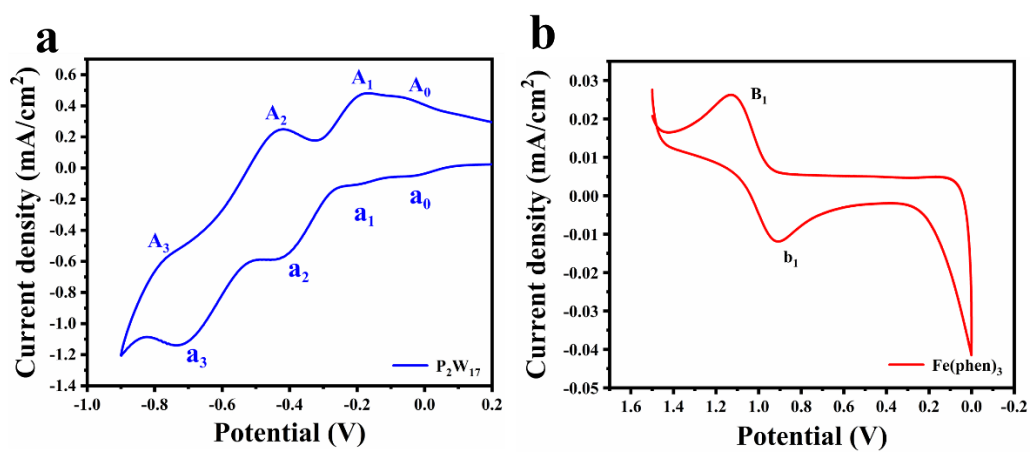


Fig. S6 CV curve of (a) P₂W₁₇ (b) Fe(phen)₃ in HOAc-NaAc solution (pH = 3.5) at 100 mV/s.

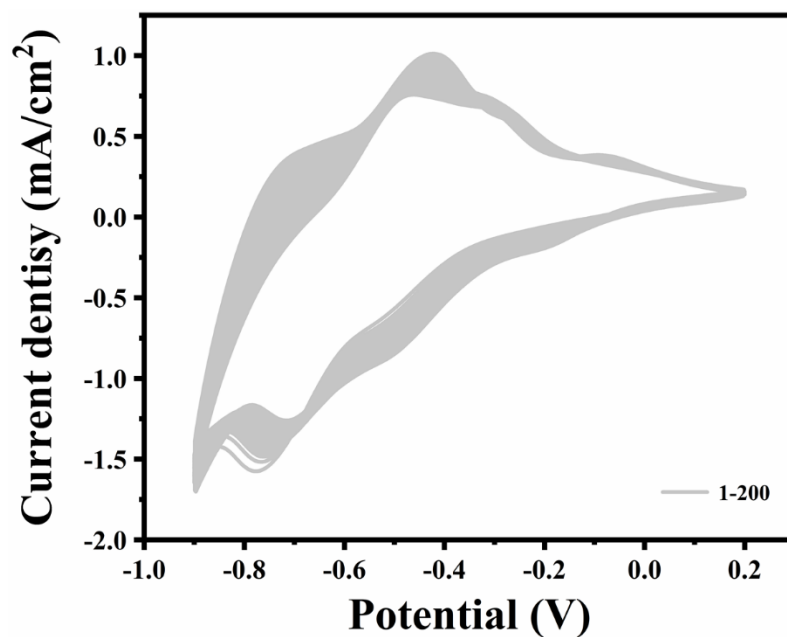


Fig. S7 CV stability of the NW/P₂W₁₇/Fe(phen)₃ composite film at 50 mV/s.

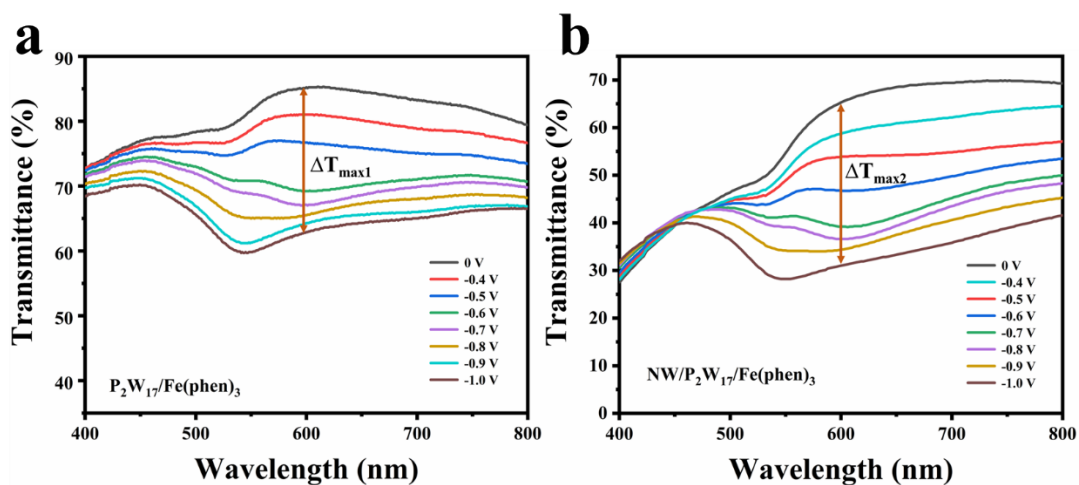


Fig. S8 Transmittance curves of (a) P₂W₁₇/Fe(phen)₃ and (b) NW/P₂W₁₇/Fe(phen)₃ composite films under different applied voltages.

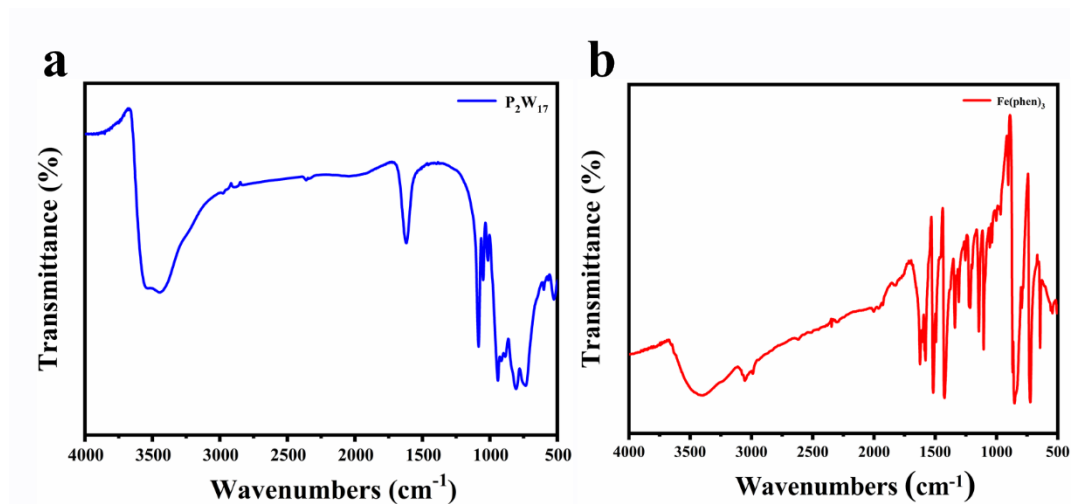


Fig. S9 (a) The IR spectra of P_2W_{17} and (b) $\text{Fe}(\text{phen})_3$.

Table S1 Comparison of electrochromic and energy storage performances of POMs-based materials

	POMs-based materials	Capacitance (F·cm ⁻³)	Coloring efficiency (cm ² /C)	Color change	Ref.
1	TiO ₂ /P ₂ W ₁₇ V	–	67.1	transparent→ blue	1
2	[P ₂ W ₁₇ /Fe(phen) ₃	–	–	orange red→light violet→ deeper violet	2
3	NW-P ₂ W ₁₇	172.3	150.34	transparent→ dark blue	3
4	NW/P ₂ W ₁₇ /Fe(phen) ₃	135.8	194.5	orange red → light blue violet → dark blue violet	Our work

1. L. Liu, S. M. Wang, C. Li, C. G. Liu, C. L. Ma and Z. B. Han, The pure inorganic multi-color electrochromic thin films: vanadium-substituted Dawson type polyoxometalates based electrochromic thin films with tunable colors from transparent to blue and purple. J. Mater. Chem. C., 2015, 3, 5175–5182.
2. G. G. Gao, L. Xu, W. Wang, W. An, Y. Qiu, Z. Wang and E. B. Wang, Electrochromic Multilayer Films of Tunable Color by Combination of Copper or Iron Complex and Monolacunary Dawson-Type Polyoxometalate, J. Phys. Chem. B., 2005, 109, 8948–8953.
3. X. S. Qu, Y. Fu, C. Ma, Y. Y. Yang, D. Shi, D. X. Chu and X. Y. Yu, Bifunctional electrochromic-energy storage materials with enhanced performance obtained by hybridizing TiO₂ nanowires with POMs, New. J. Chem., 2020, 44, 15475–15482.