

Supporting Information

Enhancing Cycling Stability of Tungsten Oxide Supercapacitor Electrodes via a Boron

Cluster-Based Molecular Cross-Linking Approach

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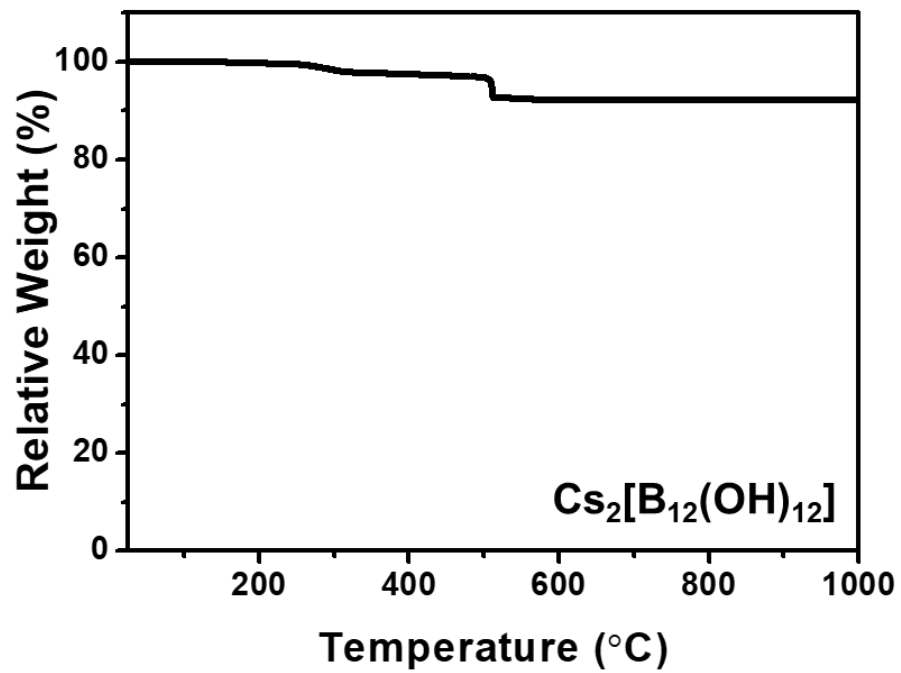


Figure S1. Thermogravimetric analysis (TGA) of $\text{Cs}_2[\text{B}_{12}(\text{OH})_{12}]$.

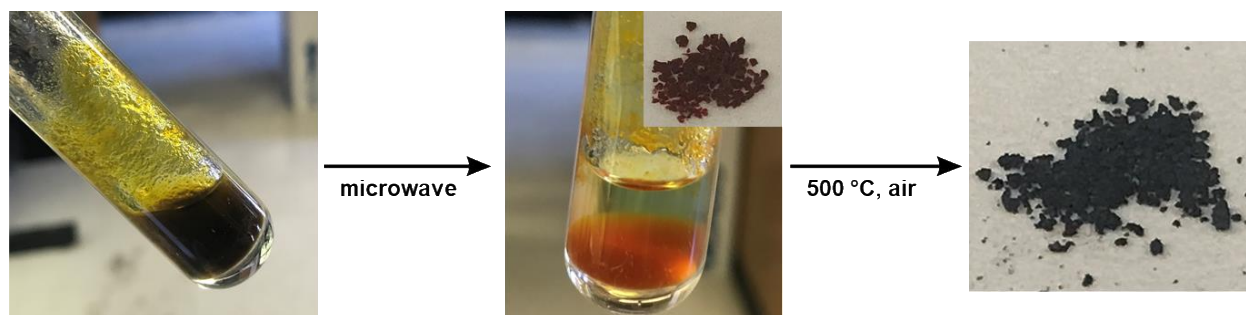


Figure S2. The optical images of synthesis of material **1**.

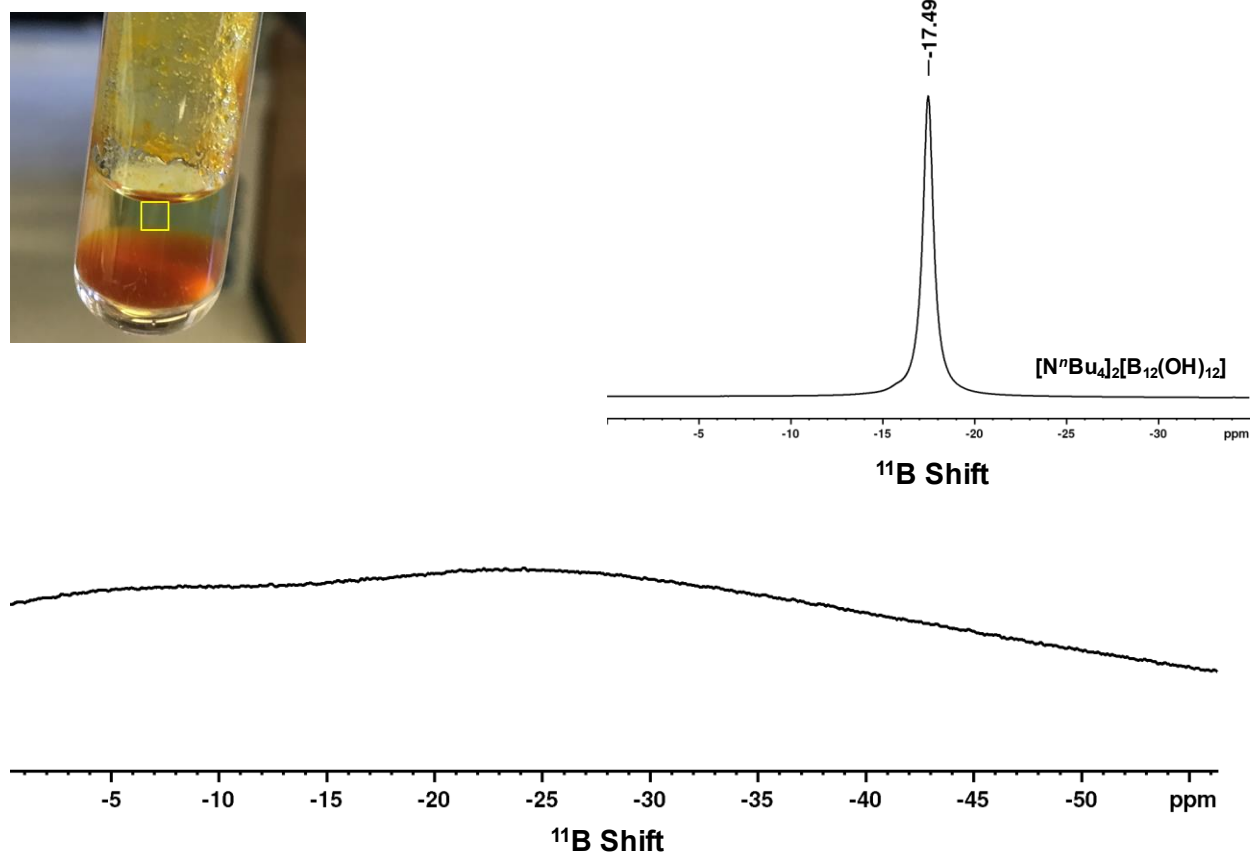


Figure S3. The ^{11}B solution NMR of the supernatant liquid after the synthesis of material **1**. (Inset) The ^{11}B NMR spectra of the $[\text{N}^n\text{Bu}_4]_2[\text{B}_{12}(\text{OH})_{12}]$ in acetonitrile- d_3 . The colorless solution further confirms the absence of radical $[\text{B}_{12}(\text{OH})_{12}]^{1-}$ species.¹

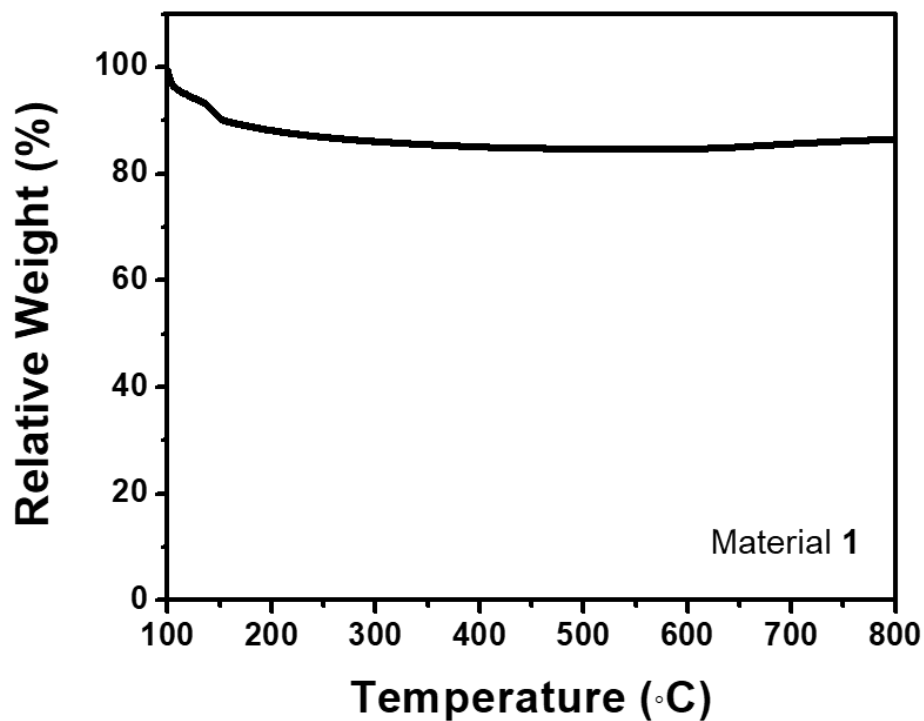


Figure S4. Thermogravimetric analysis (TGA) of material **1**.

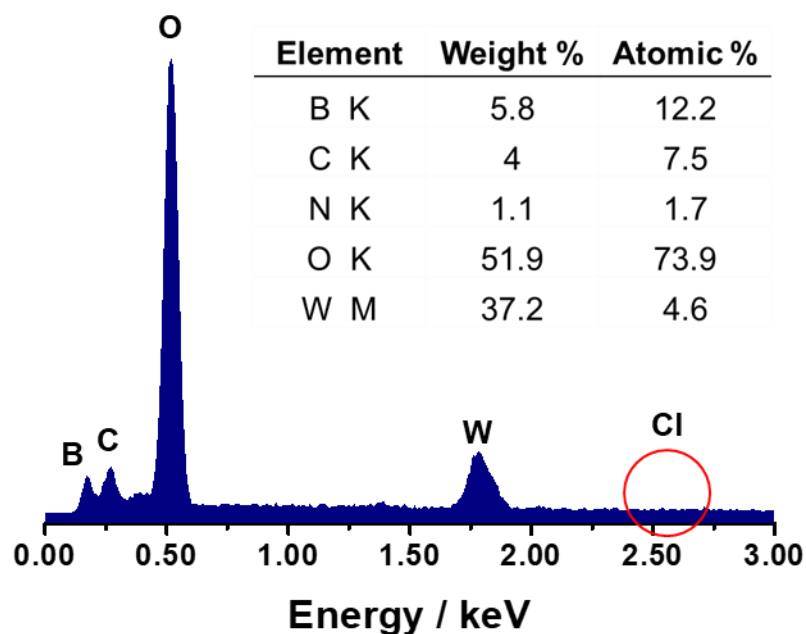


Figure S5. Energy dispersive X-ray spectroscopy (EDS) result of material **1**. (Inset) The elemental composition of material **1**. Please note that EDS is a semi-quantitative technique and these numbers do not necessarily reflect the actual elemental composition in the bulk material.

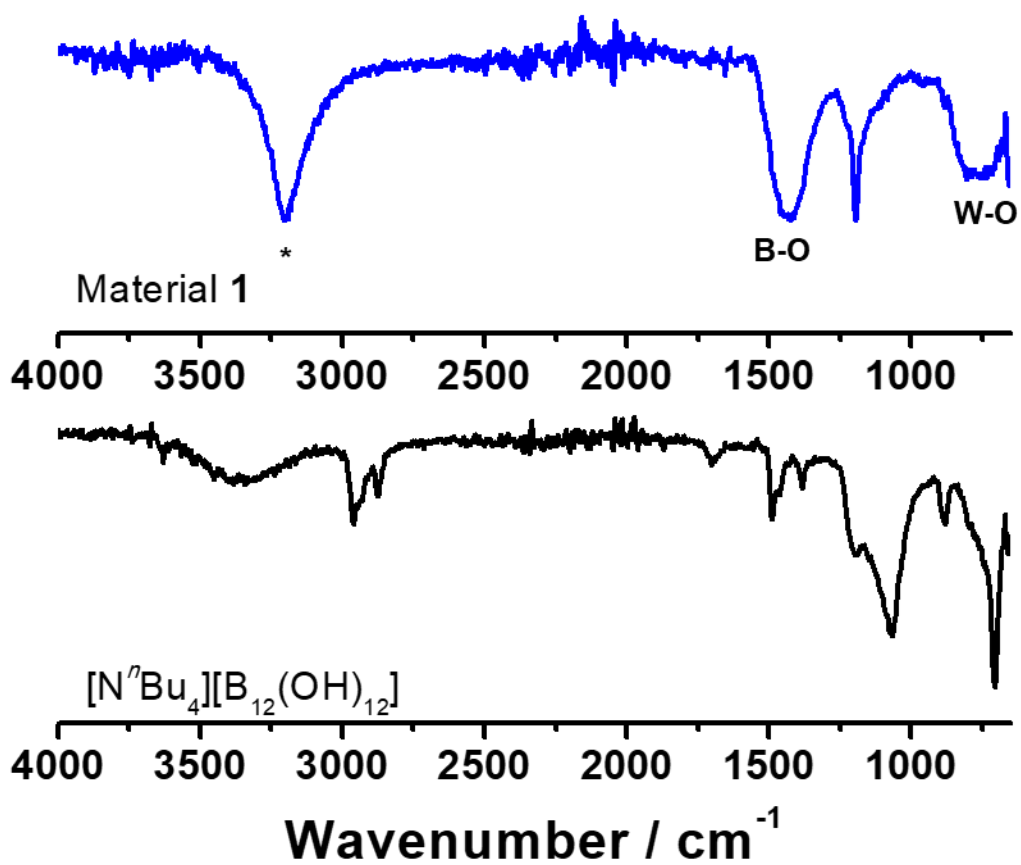


Figure S6. FT-IR spectra of material **1** (top) and $[\text{N}^n\text{Bu}_4][\text{B}_{12}(\text{OH})_{12}]$ (bottom). *The peak at $\sim 3250\text{ cm}^{-1}$ can likely arise from the surface bound water or hydroxyl groups.^{2,3}

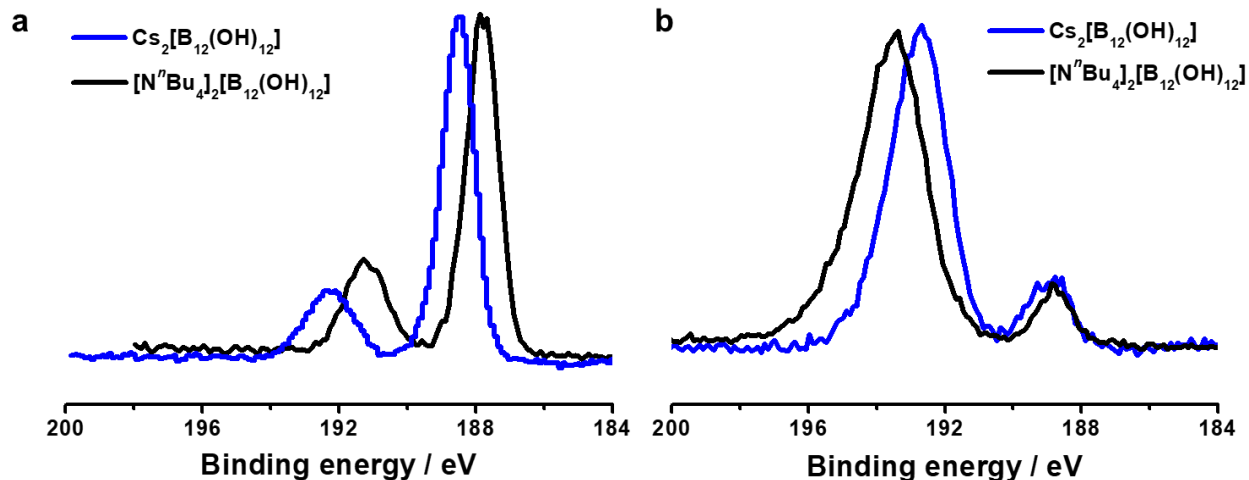


Figure S7. X-ray photoelectron spectroscopy (XPS) of (a) the pristine cross-linking agent, $[N^tBu_4]_2[B_{12}(OH)_{12}]$ and the salt $Cs_2[B_{12}(OH)_{12}]$ and (b) the annealed $[N^tBu_4]_2[B_{12}(OH)_{12}]$ and the salt $Cs_2[B_{12}(OH)_{12}]$ clusters at 500 °C.

	C 1s	O 1s	W 4f	B 1s
At %	23 %	51 %	5 %	21 %

Table S1. The elemental composition of material **1** at the surface from X-ray photoelectron spectroscopy (XPS) results.

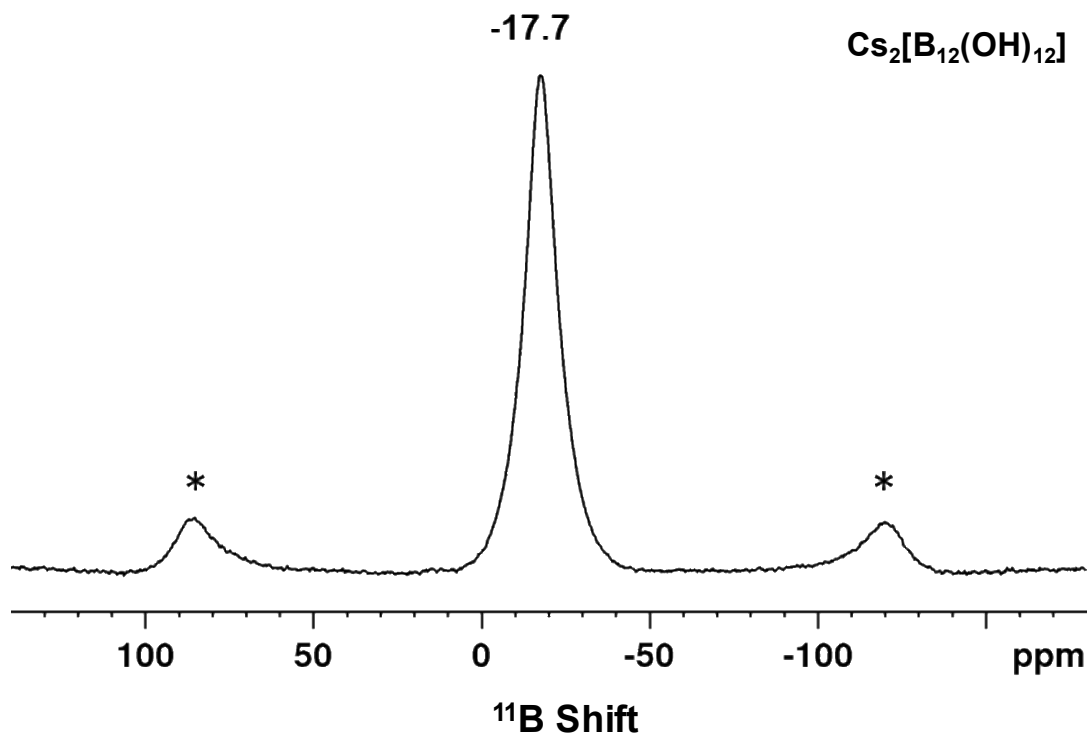


Figure S8. Solid-state 1D ^{11}B MAS NMR of $\text{Cs}_2[\text{B}_{12}(\text{OH})_{12}]$. *spinning side bands

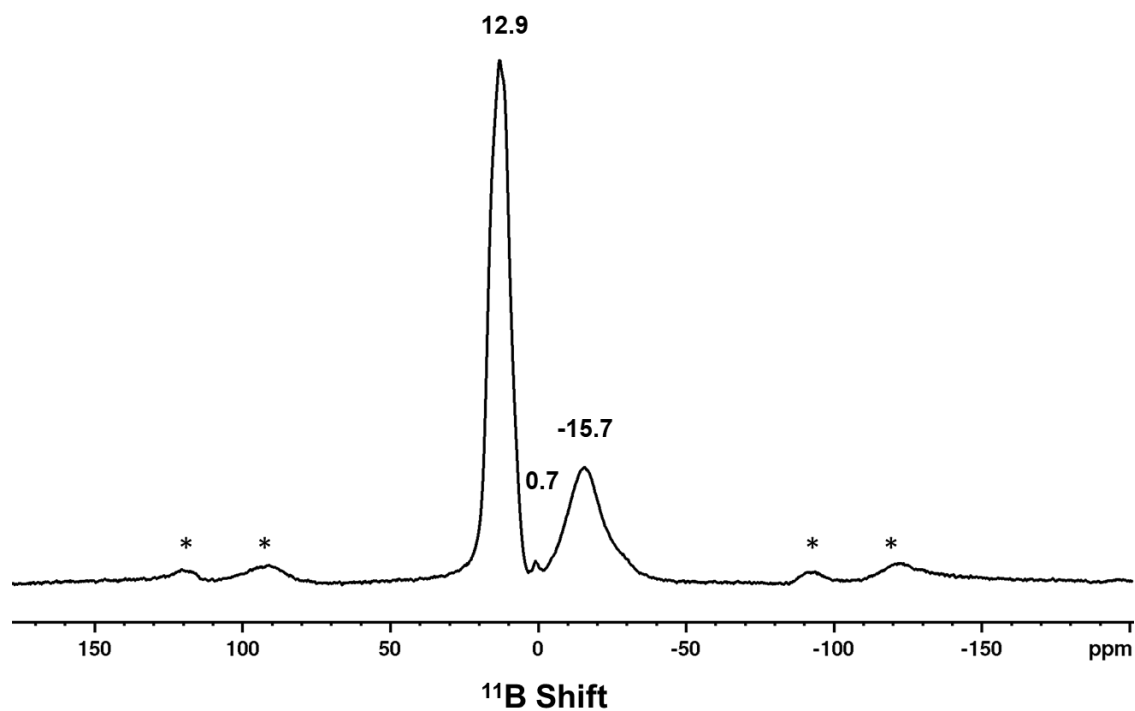


Figure S9. Solid-state 1D ^{11}B MAS NMR of material **1**. *spinning side bands

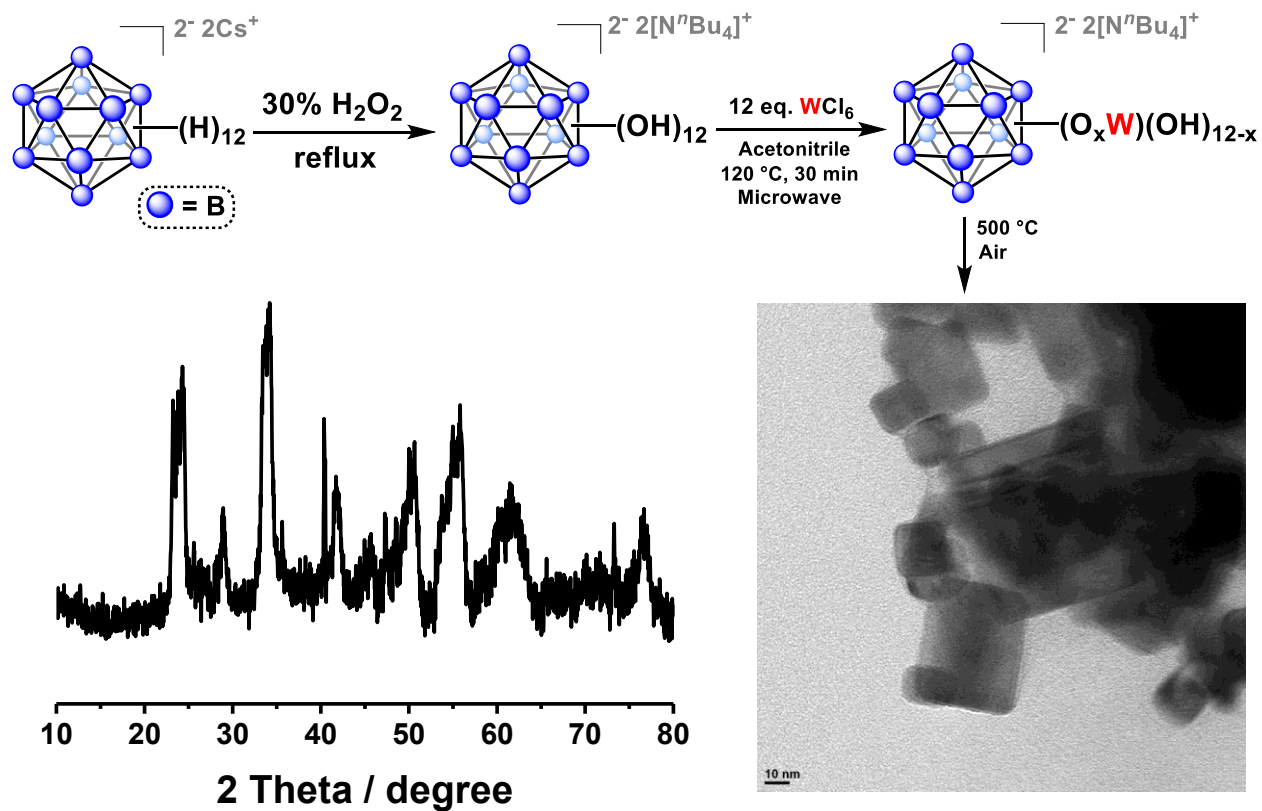


Figure S10. The synthetic route to produce material 2. $[\text{N}^n\text{Bu}_4]^+$ represents a tetrabutylammonium ion. (b) PXRD and (c) TEM image of material 2.

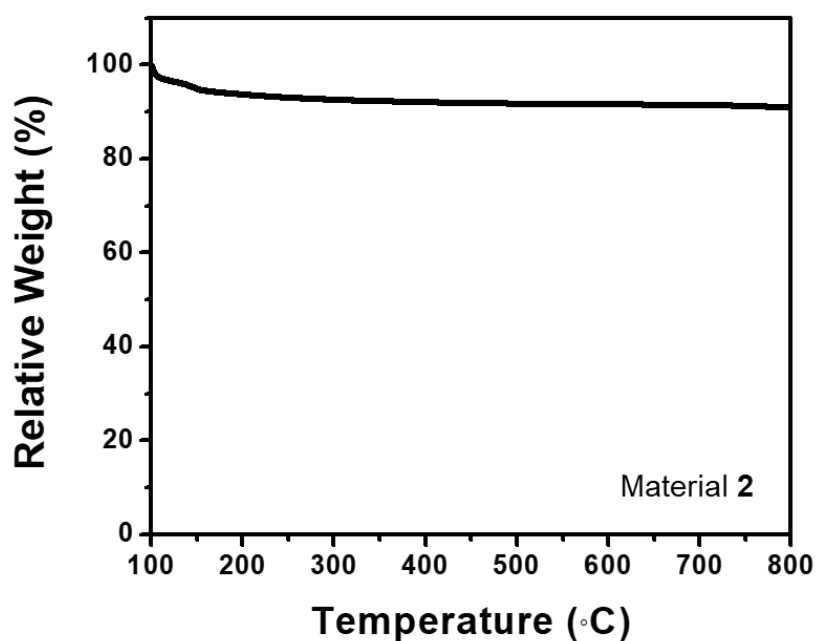


Figure S11. Thermogravimetric analysis (TGA) of material 2.

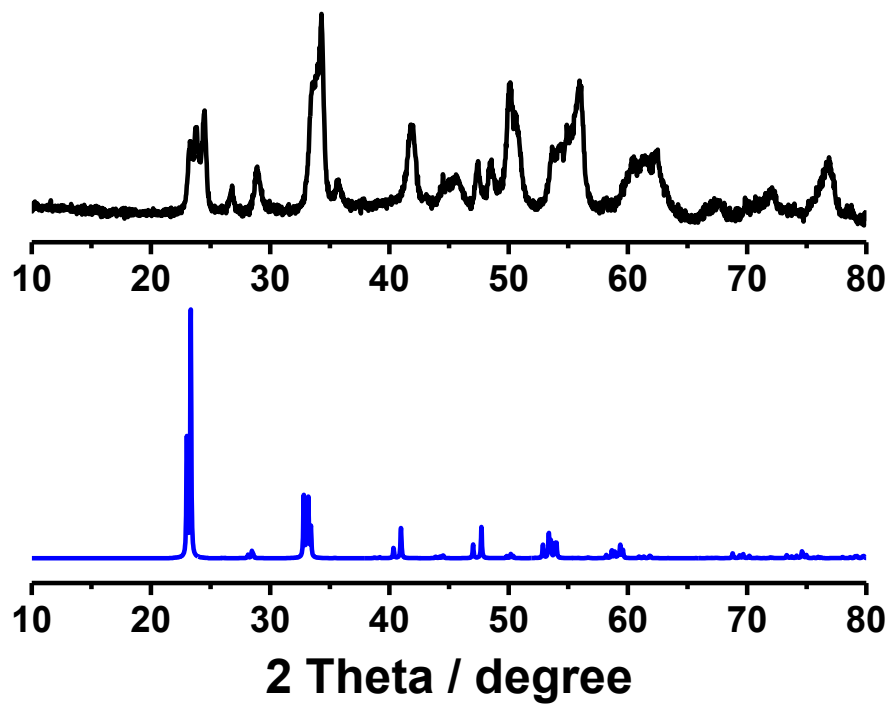


Figure S12. PXRD results of monoclinic WO_3 (top) and simulated monoclinic WO_3 .⁴

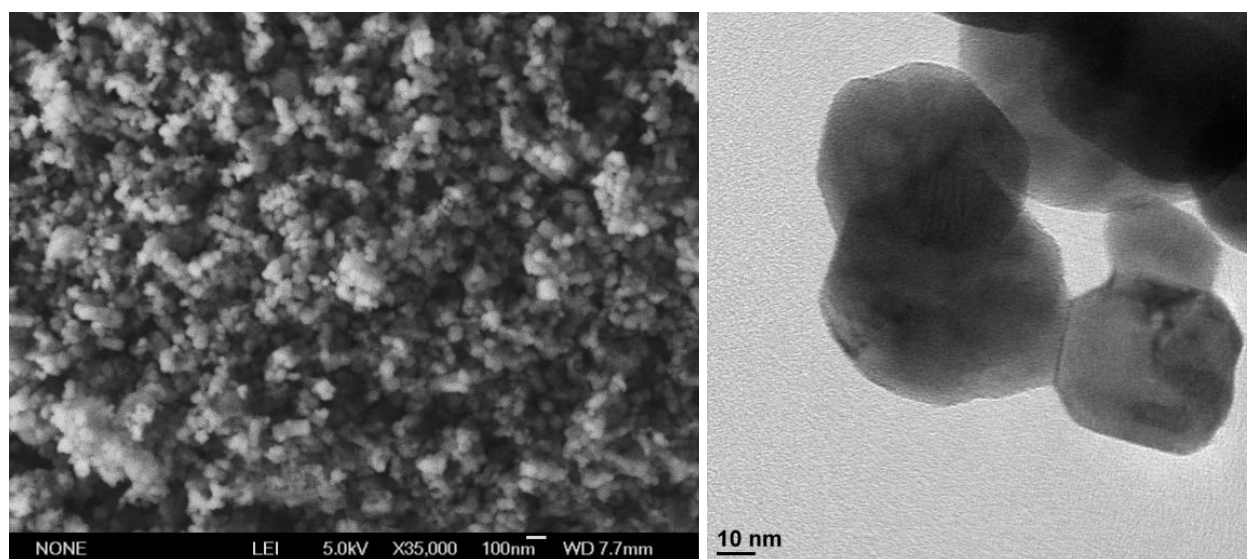


Figure S13. SEM and TEM images of monoclinic WO_3 .

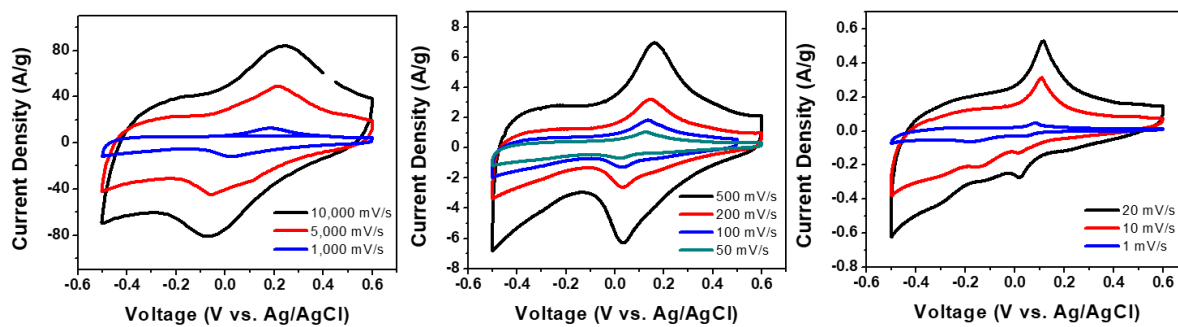


Figure S14. Cyclic voltammogram (CV) of material **1** at different scan rates.

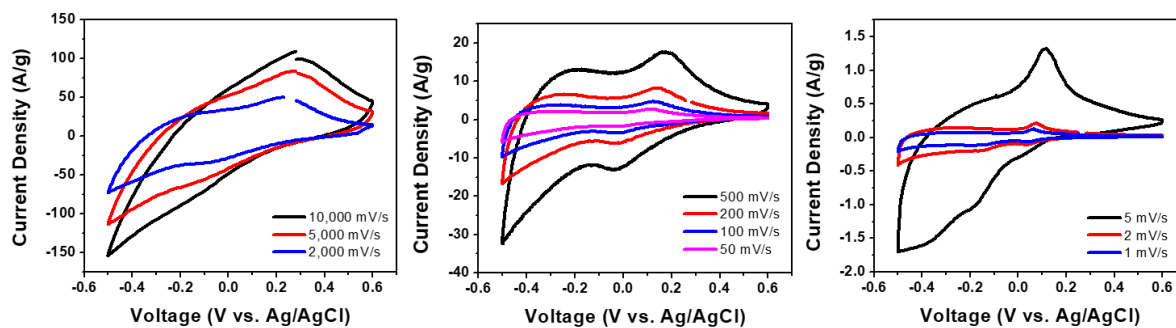


Figure S15. CV curves of material **2** at different scan rates.

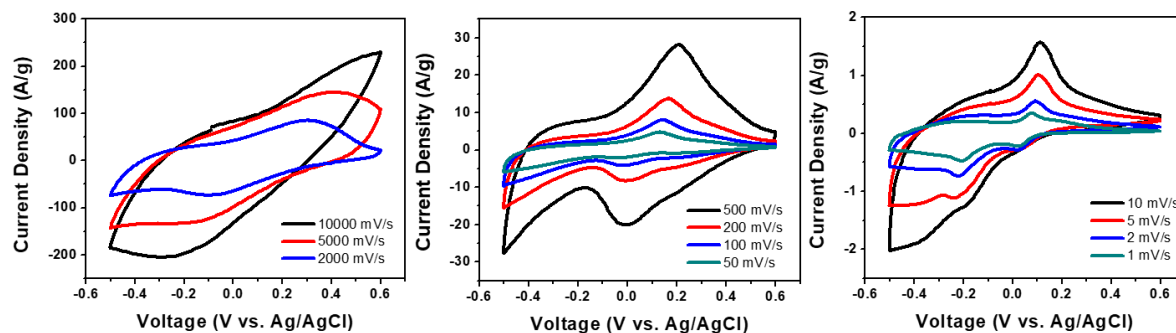


Figure S16. CV curves of m-WO₃ at different scan rates.

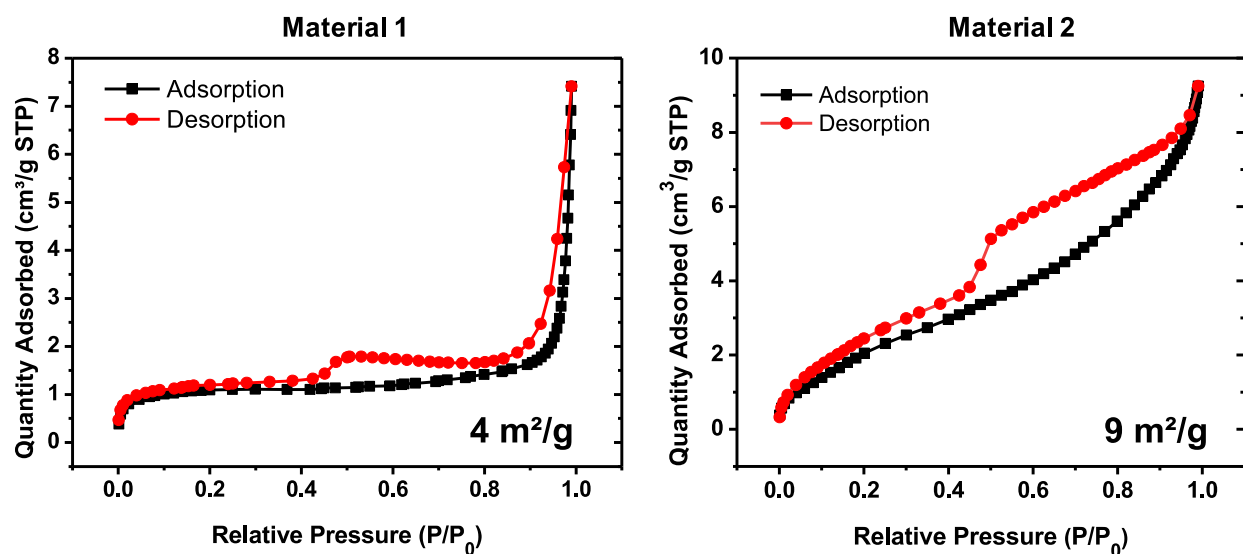


Figure S17. BET surface area of material 1 and 2.

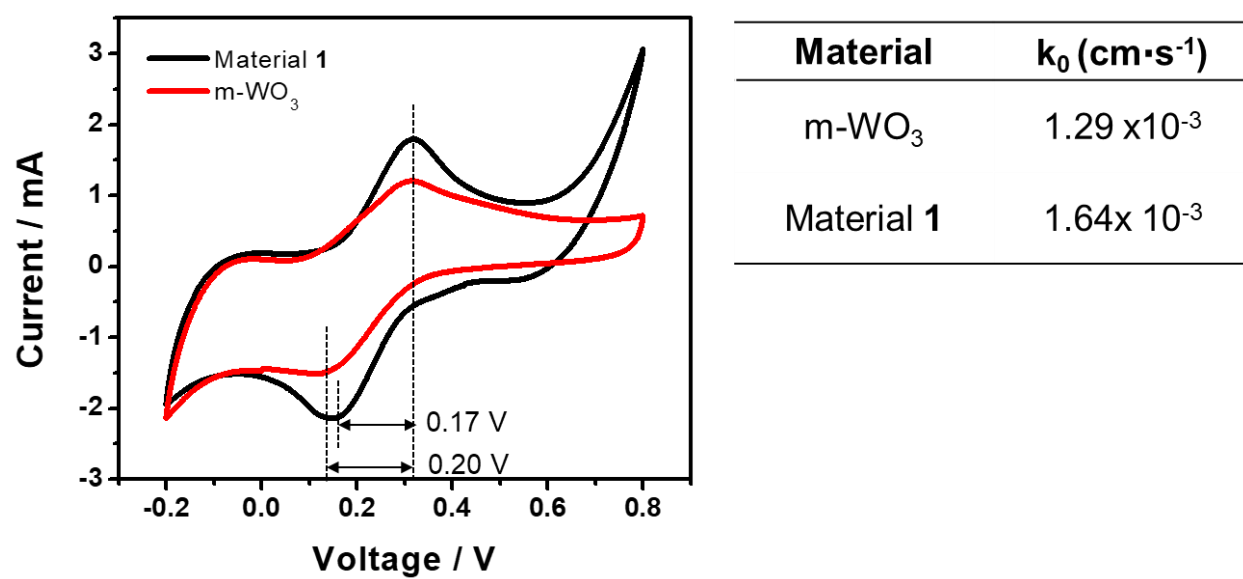


Figure S18. CV curves of material 1 and m-WO₃ for the ferri/ferrocyanide redox couple (left). The electron transfer rate constants for material 1 and m-WO₃.

References:

1. N. Van, I. Tiritiris, R. F. Winter, B. Sarkar, P. Singh, C. Duboc, A. Muñoz-Castro, R. Arratia-Pérez, W. Kaim and T. Schleid, *Chem. Eur. J.*, 2010, **16**, 11242–11245.
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3. N. Sharma, M. Deepa, P. Varshney and S. A. Agnihotry, *Thin Solid Films*, 2001, **401**, 45–51.
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