Electronic Supporting Information

Self-assembled pancake-like hexagonal tungsten oxide with ordered mesopores for supercapacitors

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We investigated the chemical stability of our pancake-like WO₃ in the aqueous H₂SO₄. This material was immersed into 0.5M H₂SO₄ solution for 20 days and the comparative SEM tests were conducted (see Fig. S1a, b, c, d, e and f). As a result, no structural and morphological change can be traced before and after immersion process. In fact, similar attempts were conducted to investigate the stability of WO₃ nanowires in 0.5M H₂SO₄ for a period of 30 days.¹ After the acid corrosion process, WO₃ exhibits the excellent stability without any structural and morphological change. After a comprehensive consideration of the two experimental results mentioned above, WO₃ can be considered to be stable in H₂SO₄ as expected. In addition, the structure stability of WO₃ can also be verified by the comparisons of the results of EIS before and after 4000 cycles. The comparative Nyquist plots were listed in Fig. S1g, which shows a similar resistance, indicating that the structure of h-WO₃ in H₂SO₄ was stable during the long-term cycles.²

The aqueous electrolyte usually consists of acid electrolyte (H_2SO_4), alkaline electrolyte (KOH) and neutral electrolyte (*i.e.* Na₂SO₄ and Li₂SO₄). The WO₃ belongs to the acid oxide, so alkaline electrolyte may not be applicable for electrochemical characterization. Of course, in the neutral electrolyte, the WO₃ is very stable, but the neutral electrolytes are not very suitable for this study based on the following reasons. 1) The need for electrochemical mechanism analysis. In our study, we tried to exhibit the difference between our nc -WO₃ and the solid h-WO₃ through charge storage mechanism analysis. Therefore, the value of redox peaks current needs to be read and used. However, according to the reported studies,³ the redox peaks of h-WO₃ can not be discernible in both Na₂SO₄ and Li₂SO₄ electrolyte. 2) The purpose for more convenient comparison. In order to facilitate discussion in the part of the mechanism analyses, we chose the same electrolyte (H₂SO₄) as the reference documentation.⁴ Thus, for this study, the aqueous H₂SO₄ electrolyte is more suitable, compared to other electrolytes.



Fig. S1 SEM images of nc-WO₃: (a, b and c) before or (d, e, f) after immersion in 0.5 M H₂SO₄ for 20 days. (g) Nyquist plots of nc-WO₃ before and after the long-term stability measurements at 50 mV s⁻¹ for 4000 cycles in 0.5M H₂SO₄.



Fig. S2 (a) SEM images of np-WO₃ under low magnification. The inset shows the SEM image under high magnification. (b) HRTEM image of np-WO₃. The inset shows the SAED result.



Fig. S3 EDS spectrum of the (a) np-WO $_3$ and (b) nc-WO $_3$

The detailed information about the pore structure from N_2 adsorption tests was listed in Table S1. And the small-angle X-ray scattering (SAXS) test for nc-WO₃ was conducted to further investigate the information on the pore structure. In short, the BET surface area and pore volume of nc-WO₃ is larger than those of np-WO₃. The mean pore size of np-WO₃ is almost 3.4 nm, possibly resulting from a stacked gap among the nanoplates, while the pore size of nc-WO₃ is almost 10.5 nm, originating from the mesopores of an individual body.

The small-angle X-ray scattering (SAXS) results for nc-WO₃ indicate that nc-WO₃ can not be defined as a typical periodic porous structure, possibly due to the existence of the non-uniform pore size and pore wall distribution, the structure defects and the ups-and-downs surface. The SAXS curve shows that a slope change exists in the range of 0.43 and 0.75 nm⁻¹, suggesting an approximate mean pore diameter of between 14.6 to 8.4 nm, according to the rough estimation formula: $D=2\pi/q$.⁵ Table S1 Textural properties of nc-WO₃ and np-WO₃.

Sample	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)						
nc–WO₃	32.41	0.074	10.5						
np–WO ₃	11.04	0.031	3.4						



Fig. S4 SAXS result for nc-WO₃.



Fig. S5 SEM results of nc-WO₃ before annealing.

The structures of pancake-like WO₃ before and after annealing were further characterized using FTIR spectroscopy and the results in the spectral range of 400-4000 cm⁻¹ are showed in Fig. S6c. A broad peak at around 3434 cm⁻¹ is assigned to the stretching vibration of water molecule.⁶ The peaks at ~ 1625-1638 cm⁻¹ represent the bending vibration mode of water molecule and the peaks at ~1384 cm⁻¹ that of hydroxyl molecule. There is no obvious change in the strength of these peaks. The peak at ~ 660-877 cm⁻¹ is the O-W-O stretching mode and that at ~1049 cm⁻¹ is the W-O stretching mode respectively.^{6,7} Noting that the peaks, resulting from O-W-O stretching mode, shifted a little to the higher wave number as annealing was employed.



Fig. S6 (a) XRD results of nc-WO₃ before and after annealing. (b) The enlarged XRD patterns of nc-WO₃ before and after annealing between $2\theta=22^{\circ}$ to 24° . (c) FTIR results of nc-WO₃ before and after annealing.



Fig. S7 SEM images of WO $_3$ with different PH value: (a and b) PH=1, (c and d) PH=2.5.



Fig. S8 SEM images of WO_3 with the addition of (a and b) 0.32 g and (c and d) 2.64 g Na_2WO_4 .



Fig. S9 CV curves of np-WO $_3$ at different scan rates.

Table S2 Comparison of synthesis method, crystal structure, morphology, voltage window, Loading mass, electrolyte, reference electrodes and specific capacitance between nc-WO₃ and as-reported WO₃-based electrodes.

Formula	synthesis	crystal	Morphology	Voltage	Loading	electrolyte	reference	Cs	I	Ref.
	method	structure		window	mass		electrodes	(F g ⁻¹)	(Ag-1)	
h-WO₃	hydrothermal	hexagonal	Pancake	-0.3-0.2	4.0	0.5 M H ₂ SO ₄	Ag/AgCl	605.5	0.37	In this
			-like							work
h-WO₃	hydrothermal	hexagonal	Aligned	-0.5-0	N/A	0.5 M H ₂ SO ₄	SCE	421.8	0.5	4
			nanopillar							
h-WO₃	hydrothermal	hexagonal	nanowire	-0.5-0.2	4.0	1.0 M H ₂ SO ₄	SCE	428	1	8
h-WO₃	hydrothermal	hexagonal	Nanorod	-0.65-0.	3.6	1.0 M H ₂ SO ₄	SCE	385	0.5	9
			-bundles	2						
h-WO₃	hydrothermal	hexagonal	cactus-like	0-0.6	1.8	1.0 M	Ag/AgCl	485	0.5	10
			spheres			Na_2SO_4				
h-WO₃	hydrothermal	hexagonal	nanorods	-0.41-0	N/A	0.5 M H ₂ SO ₄	Ag/AgCl	319.26	0.7	11
h-WO₃	hydrothermal	hexagonal	nanorod	-0.1-0.7	N/A	1.0 M	Ag/AgCl	463	1	12
			arrays			Na_2SO_4				
$WO_3 \cdot H_2O$	hydrothermal	orthorhomb	flower-like	-0.4-0.1	N/A	1.0 M H ₂ SO ₄	SCE	244	1	13
/ rGO		ic								
WO₃@Cu	hydrothermal	triclinic	microsphere	0-0.5	N/A	6.0 M KOH	SCE	248.2	1	14
0			S							



Fig. S10 CV, GCD and long-term results of nc-WO₃ under the potential window of 1V.

References

- 1. C. Jo, J. Lee, C. W. Lee and S. Yoon, J. Phys. Chem. C 2011, 115, 11880-11886.
- 2. X. Chen, Y. Zhang, X. Sun, Adv. Energy Mater., 2016, 26, 8126-8132.
- 3. Z. Chen, Y. Peng, F. Liu, Z. Le, J. Zhu, G. Shen, D. Zhang, M. Wen, S. Xiao, C. P. Liu, Y. Lu and H. Li, *Nano Lett.*, 2015, **15**, 6802-6808.
- 4. M. Zhu, Y. Huang, Y. Huang, and C. Zhi, ACS Appl. Mater. Interfaces, 2014, 6, 18901-18910.
- 5. M.V. Avdeev and L. Rosta, *Diamond Relat. Mater.* , 2007, 16, 2050-2053.
- D. Susanti, L. Tananta, H. Purwaningsih, R. Fajarin, and G.E. Kusuma, *Front. Mater. Sci.*, 2013, 7, 70–378.
- 7. R. Yuksel, C. Durucan and H. E. Unalan, J. Alloys Compd., 2016, 658, 183-189.
- X. Yuan, B. Chen, X. Wu, J. Mo, Z. Liu, Z. Hu, Z. Liu, C. Zhou, H. Yang and Y. Wu, *Chin. J. Chem.*, 2017, 35, 61-66.
- 9. H. Peng, K. Sun, J. Mu, M. Luo, Z. Lei, *Electrochim. Acta*, 2014, 147, 54-61.
- 10. F. Zheng, H. Gong, Z. Li, W. Yang, J. Xu, P. Hu, Y. Li, Y. Gong and Q. Zhen, *J. Alloys Compd.*, 2017, **712**, 345-354.
- 11. S. Yao, F. Qu, G. Wang and X. Wu, J. Alloys Compd., 2017, 724, 695-702.
- 12. F. Zheng, S. Song, F. Lu, R. Li, N. Bu, J. Liu, Y. Li, P. Hu and Q. Zhen, *CrystEngComm*, 2016, **18**, 3891-3904.
- 13. L. Ma, L. Xu, X. Xu, L. Zhang, C. Ye, J. Luo, W. Chen, *Colloids Surf. A*, 2015, **481**, 609-615.
- 14. J. Tian, B. Lin, Y. Sun, X. Zhang and H. Yang, Mater. Lett., 2017, 206, 91-94.