Supporting information

Amorphous Cr₂WO₆ Modified WO₃ nanowires with Large Specific Surface Area and Rich Lewis Acid Sites: a Highly Efficient Catalyst for Oxidative Desulfurization

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Figure S1. The SEM image of *pure* WO₃ bundles obtained without Cr³⁺ cations.



Figure S2. The SEM images of (a, a1) a-Cr₂WO₆-180°C-12h, (b, b1) Cr₂WO₆-180°C-24h and (c, c1) Cr₂WO₆-200°C-24h; (d) The XRD patterns, (e) Raman spectra and (f) FT-IR spectra of above three samples synthesized with the Cr/W molar ratio of 2.

Three products were synthesized by using sodium tungstate and chromium acetate as raw materials under different conditions, and their SEM images are presented in **Figure S2 (a-c, a1-c1)**. It can be seen that they are all irregular nanoparticles, and the size of nanoparticles grows up gradually with extension of reaction time and increase of reaction temperature. In their XRD patterns (**Figure S2d**), the amorphous sample is obtained after reaction at 180 °C for 12 h. The Cr_2WO_6 with certain crystallinity can be obtained by prolonging the reaction time (180 °C for 24 h), and its crystallinity further increases at 200 °C for 24 h. In addition, the samples have the same Raman and FT-IR characteristic peaks in **Figure S2e** and **Figure S2f**, respectively. Therefore, the three samples obtained under different conditions have the same phase, and the product synthesized at 180 °C for 12 h is amorphous Cr_2WO_6 (*a*- Cr_2WO_6).



Figure S3. The FT-IR spectra of *pure* WO₃, commercial Cr_2O_3 (*c*- Cr_2O_3), *a*- Cr_2WO_6 and *a*- Cr_2WO_6/WO_3 samples.

Figure S3 presents the FT-IR spectra of *pure* WO₃, commercial Cr_2O_3 (*c*- Cr_2O_3), *a*- Cr_2WO_6 and *a*- Cr_2WO_6/WO_3 samples. For all samples, the absorption band at 3000-3700 cm⁻¹ and the peak at 1630 cm⁻¹ are corresponding to the stretching and bending vibration of -OH from adsorbed water, and the peak at 1389 cm⁻¹ is indexed to the bending vibration of surface -OH groups, respectively. For *pure* WO₃, the peak at 833 cm⁻¹ and band at 685 cm⁻¹ can be ascribed to the stretching mode of O-W-O bond. The strong absorption peak at 621 cm⁻¹ and 569 cm⁻¹ are attributed to the stretching modes of O-Cr-O bond in *c*-Cr₂O₃ sample. The *a*-Cr₂WO₆ and *a*-Cr₂WO₆/WO₃ have similar weak absorption peaks at 833 cm⁻¹ (O-W-O) and 569 cm⁻¹ (O-Cr-O), but their relative intensities are different, the relative intensity of O-W-O in *a*-Cr₂WO₆/WO₃ is significantly higher than that in *a*-Cr₂WO₆, revealing that the WO₃ is the main phase in *a*-Cr₂WO₆/WO₃ sample. The broad absorption band at 900-1100 cm⁻¹ is indexed to M=O bond for different samples.



Figure S4. N_2 adsorption-desorption isotherms of (a) *pure* WO₃ bundles, (b) *a*-Cr₂WO₆ nanoparticles and their corresponding pore size distributions.



Figure S5. The TEM images of a-Cr₂WO₆/WO₃ nanowires in different areas of a) and b).



Figure S6. The (a) TEM, (b) HRTEM images and SAED pattern (inset b) of *pure* WO₃ bundles.



Figure S7. The extraction efficiency of MeCN: m(MeCN)/m(oil)=1:4, ambient temperature.



Figure S8. The SEM images of low magnification for samples obtained with different Cr/W mole ratio and corresponding Cr contents in EDX. The Cr/W mole ratio is (a) 0, (b) 0.03, (c) 0.05, (d) 0.10 and (e) 0.20; (f) The XRD patterns of above five samples.



Figure S9. The FT-IR-Py spectra of samples with different Cr/W mole ratio of 0, 0.03, 0.05, 0.10 and 0.20 at 100 °C (a) and 200 °C (b).

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Temperature	100 °C			200 °C			
Samples	C _B	C_{L}	C _{Total}	C _B	C_{L}	C _{Total}	
Cr/W-0 (pure							
WO ₃)	-	-	-	-	-	-	
Cr/W-0.03	11.5	17.6	29.1	4.9	10.2	15.1	
Cr/W-0.05	28.5	55.2	83.7	10.7	39.7	50.4	
Cr/W-0.10	58.5	128.4	186.9	31.7	95.5	127.3	
Cr/W-0.20	53.0	159.5	212.5	28.1	126.8	154.9	

Table S1. Surface acidic sites per g of samples with different Cr/W mole ratio of 0, 0.03, 0.05, 0.10 and 0.20 determined by FT-IR-Py spectra (μ mol·g⁻¹).

Table S2. The ODS performance of DBT with as-synthesized a-Cr₂WO₆/WO₃ nanowires and reported WO₃ based catalysts.

Catalysts	ppm	mode oil	Cat.	Т	t ^[b]	С	activity ^[c]	reference
		(mL)	(mg)	(°C)	(min)	(%)	µg∙mg ⁻¹ ∙min ⁻¹	
WO _x /ZrO ₂	490 ^[a]	50	100	60	60	100	4.0	[1]
WO _x /TiO ₂	2000	14	100	50	60	98	4.5	[2]
WO ₃ /g-C ₃ N ₄	500	5	20	60	180	91.2	0.63	[3]
	500	5	50	50	40	91.0	1.1	[4]
W- <i>m</i> -silica	500	5	25	60	20	97.1	4.85	[5]
WO ₃ /SBA-15	540	20	40	60	80	91	3.0	[6]
WO ₃ /Fe ₃ O ₄	500 ^[a]	5	10	100	270	92.3	0.60	[7]
WO ₃ /CNT-2	800 ^[a]	5	30	50	60	90.7	1.4	[8]
WO ₅ /2MoO ₅ -CNT	300	5	56	60	45	98	0.58	[9]
W ₁₈ O ₄₉ -MC	500	5	10	70	40	99	6.1	[10]
U-WO ₃ NBs	174	50	90	50	60	96	2.78	[11]
Mesoporous WO ₃	2000	14	100	50	60	100	3.2	[12]
WO _x -OAm-HCl	500	5	10	60	30	100	5.8	[13]
F-WO ₃ ·H ₂ O	4000 ^[a]	20	126	70	60	95.0	7.0	[14]
a-Cr ₂ WO ₆ /WO ₃	870 ^[a]	12.6	60	70	50	96.2	3.3	Our
	2600 [a]	13.0			60	94.0	8.1	work

[a]: The unit of ppm is $\mu g \cdot g^{-1}$.

[b]: The t is the time when reaction equilibrium begins.

[c]: The activity=the mass of converted DBT/(reaction time×dosage of catalyst).



Figure S10. (a-c) The ODS of BT, DBT and 4,6-DMDBT with *a*-Cr₂WO₆/WO₃ nanowires at different temperatures (40 °C, 50 °C, 60 °C, 70 °C) and (a1-c1) their fitting lines of $\ln(C_0/C_t)$ -time (t) before 60 min.

S-16	Temperature	$V \rightarrow 10^{-2} (\dots \dots \dots 1)$	R ²	
Sulfur source	(°C)	$K_{ODS} \times 10^{-2} \text{ (mm^{-1})}$		
BT	40	0.235	0.979	
	50	0.470	0.990	
	60	0.815	0.990	
	70	1.758	0.996	
DDT	40	0.857	0.989	
	50	1.867	0.986	
DDI	60	1.758 0.857 1.867 2.891 5.891	0.998	
	70	5.891	0.996	
4, 6-DMDBT	40	0.238	0.970	
	50	0.546	0.982	
	60	1.001	0.995	
	70	1.916	0.991	

Table S3. The reaction rate constant (K_{ODS}) and correlation coefficient (R^2) for oxidation reaction of BT, DBT and 4, 6-DMDBT at different temperatures.



Figure S11. (a, b) The SEM images and (c) N_2 adsorption-desorption isotherm of used *a*-Cr₂WO₆/WO₃ nanowires, (d) XRD patterns, (e) Cr 2p and (f) W 4f XPS spectra of fresh and used *a*-Cr₂WO₆/WO₃ nanowires.



Figure S12. The optical photograph of a-Cr₂WO₆/WO₃ nanowires synthesized on a large scale.



Figure S13. The products of BT, DBT and 4, 6-DMDBT in ODS process with a-Cr₂WO₆/WO₃ nanowires.



Figure S14. The FT-IR spectrum of the crystalline product in ODS of BDT.



Figure S15. The UV-Vis spectra of a-Cr₂WO₆/WO₃ nanowires mixed with H₂O and H₂O₂.



Figure S16. The S 1s XPS spectrum of used *a*-Cr₂WO₆/WO₃ nanowires.

References

- Rodriguez-Gattorno, G.; Galano, A.; Torres-García, E. Surface Acid-Basic Properties of WO_x-ZrO₂ and Catalytic Efficiency in Oxidative Desulfurization. *Appl. Catal., B* 2009, 92, 1-8.
- (2) Li, Z.; Hong, G. H.; Park, J. S.; Sivaranjani, K.; Li, C.; Park, S. B.; Song, B. J.; Yoon, J.; Lee, C. W.; Kim, J. M. Catalytic Oxidative Desulfurization of Dibenzothiophene Compounds over Tungsten Oxide Catalysts Supported on Spherical Mesoporous TiO₂. *Sci. Adv. Mater.* 2017, 9, 1236-1240.
- (3) Zhao, R.; Li, X.; Su, J.; Gao, X. Preparation of WO₃/g-C₃N₄ Composites and Their Application in Oxidative Desulfurization. *Appl. Surf. Sci.* 2017, 392, 810-816.
- (4) Ma, R.; Guo, J.; Wang, D.; He, M.; Xun, S.; Gu, J.; Zhu, W.; Li, H. Preparation of Highly Dispersed WO₃/Few Layer g-C₃N₄ and Its Enhancement of Catalytic Oxidative Desulfurization Activity. *Colloids Surf.*, A 2019, 572, 250-258.
- (5) Shen, D.; Dai, Y.; Han, J.; Gan, L.; Liu, J.; Long, M. A Nanocellulose Template Strategy for the Controllable Synthesis of Tungsten Containing Mesoporous

Silica for Ultra-Deep Oxidative Desulfurization. Chem. Eng. J. 332 (2018) 563-571.

- (6) Li, X.; Huang, S.; Xu, Q.; Yang, Y. Preparation of WO₃-SBA-15 Mesoporous Molecular Sieve and Its Performance as an Oxidative Desulfurization Catalyst. *Transition Met. Chem.* 2009, 34, 943-947.
- (7) Feng, Z.; Zhu, Y.; Zhou, Q.; Wu, Y.; Wu, T. Magnetic WO₃/Fe₃O₄ as Catalyst for Deep Oxidative Desulfurization of Model Oil. *Mater. Sci. Eng.*, B 2019, 240, 85-91.
- (8) Wang, C.; Li, A.; Xu, J.; Wen, J.; Zhang, H.; Zhang, L. Preparation of WO₃/CNT Catalysts in Presence of Ionic Liquid [C₁₆mim]Cl and Catalytic Efficiency in Oxidative Desulfurization. *J. Chem. Technol. Biotechnol.* 2019, 94, 3403-3412.
- (9) Afsharpour, M.; Dini, Z. One-Pot Functionalization of Carbon Nanotubes by WO₃/MoO₃ Nanoparticles as Oxidative Desulfurization Catalysts. *Fuller*. *Nanotub. Car. N.* 2018, 27, 198-205.
- (10)Sun, H.; Wu, P.; He, J.; Liu, M.; Zhu, L.; Zhu, F.; Chen, G.; He, M.; Zhu, W. Fabrication of Oxygen-Defective Tungsten Oxide Nanorods for Deep Oxidative Desulfurization of Fuel. *Petrol. Sci.* 2018, 15, 849-856.
- (11)He, J.; Liu, H.; Xu, B.; Wang, X. Highly Flexible Sub-1 nm Tungsten Oxide Nanobelts as Efficient Desulfurization Catalysts. *Small* 2015, 11, 1144-1149.
- (12)Li, Z.; Jeong, H. J.; Sivaranjani, K.; Song, B. J.; Park, S. B.; Li, D.; Lee, C. W.; Jin, M.; Kim, J. M. Highly Ordered Mesoporous WO₃ with Excellent Catalytic Performance and Reusability for Deep Oxidative Desulfurization. *Nano* 2015, 10, 1550075-1550082.
- (13)He, J.; Wu, P.; Wu, Y.; Li, H.; Jiang, W.; Xun, S.; Zhang, M.; Zhu, W.; Li, H. Taming Interfacial Oxygen Vacancies of Amphiphilic Tungsten Oxide for Enhanced Catalysis in Oxidative Desulfurization. ACS Sustainable Chem. Eng. 2017, 5, 8930-8938.
- (14)Xiao, X.; Zhong, H.; Zheng, C.; Lu, M.; Zuo, X.; Nan, J. Deep Oxidative Desulfurization of Dibenzothiophene Using a Flower-Like WO₃·H₂O Catalyst in

an Organic Biphasic system. Chem. Eng. J. 2016, 304, 908-916.