**Supplementary information** 

## Confined interfacial micelle aggregating assembly of ordered macro-mesoporous tungsten oxides for H<sub>2</sub>S sensing

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Fig. S1 SEM image of  $SiO_2$  photonic crystals (PCs).



Fig. S2 TEM image of the PEO-*b*-PS/W(AcAc)<sub>6</sub> spherical micelles.



Fig. S3 SEM (a, c) and TEM (b, d) images of the structure and morphology of the tungsten oxide as a function of reaction time, 60 min (a, b) and 120 min (c, d).



Fig. S4 SEM image of SiO<sub>2</sub> PCs/WO<sub>3</sub> composites



Fig. S5 TEM images (a-c) of the ordered macro/mesoporous carbon after etching out  $SiO_2$  and  $WO_3$ , STEM image (d) and corresponding element distribution (e-g).



Fig. S6 SEM (a-c), TEM (d-f) taken along at different facets [110] (d), [211] (e) and [111] (f), and HRTEM (g) images of mesoporous  $WO_3$ . The insets in d and e are the corresponded fast Fourier transform and selected area electron diffraction, respectively.



Fig. S7 SEM (a, b) and TEM (c, d) images of macroporous WO<sub>3</sub>.



Fig. S8 XPS core-level spectra of O 1s (a) and W 4f (b) for porous  $WO_3$  materials.



Fig. S9. Response–recovery curve of OMMW (a), mesoporous  $WO_3$  sensor (b) and macroporous  $WO_3$  sensor (c) toward  $H_2S$  with different concentrations and dynamic response–recovery curve of macroporous  $WO_3$  (c) toward 50 ppm of  $H_2S$ .



Fig. S10. Response of the sensors toward different H<sub>2</sub>S concentration based on the three WO<sub>3</sub>-based sensor (c)



Fig. S11. Responses of OMMW to 1–100 ppm  $H_2S$  at different relative humidity.



Fig. S12 Response–recovery curve of ordered macro-mesoporous  $WO_3$  nanostructures toward  $H_2S$  with an ultralow concentration (a), response and recovery curve of OMMW toward 50 ppm of  $H_2S$  for seven cycles (b), and stability test toward 50 ppm of  $H_2S$  for 30 days (c).



Fig. S13 SEM and TEM image of OMMW after the cycle gas sensing test

Table S1 Physical properties of WO<sub>3</sub>.

Materials	Surface area (m² g⁻¹)	Pore size (nm)	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	
OMMW	78	34.1	0.24	
Mesoporous WO <sub>3</sub>	98	19.4	0.13	
Macroporous WO <sub>3</sub>	35	59.2	0.08	

Table S2. Comparison of H <sub>2</sub> S sensing performances	

Materials and	Concentratio	Sensitivity	Response/recover	Detection	Ref
morphology	n (H₂S)	(Ra/Rg)	y time(s)	limit	
SnO2/rGO/PANI	5 ppm	4.3	121/117	0.05	[4]
Porous ZnO hollow	100 ppb	2<	>29/>98	10 ppb	[47]
tubule					
Fe <sub>2</sub> O <sub>3</sub> nanoboxes	5 ppm	6	31/187	0.25	[48]
Flower-like WO <sub>3</sub>	20 ppm	10.9	0.9/19	0.3	[16]
Mesoporous WO <sub>3</sub>	50	262	2/38	0.25	[30]
WO₃ nanotube	5 ppm	11.45	>10/>120	0.03	[49]
WO <sub>3</sub> microbelts	5 ppm	11.7	8/260	0.4	[50]
V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub>	60 ppm	22.3	155/148	5 ppm	[51]
Flower-like WO <sub>3</sub> /CuO	5 ppm	105	42/10	0.25	[52]
Net-like SnO <sub>2</sub> /ZnO	5 ppm	112	>500/>40s	0.1ppm	[53]
Macroporous WO <sub>3</sub>	50 ppm	82	7/18	0.25 ppm	This work
OMMW	50 ppm	216	4/20 (s)	0.25 ppm	This work