Electronic Supplementary Information for

Synthesis mechanism and gas-sensing application of nanosheet-assembled tungsten oxide microspheres†

Shouli Bai,[a] Kewei Zhang,[a] Liangshi Wang,[b] Jianhua Sun,[ac] Ruixian Luo,*[a] Dianqing Li*[a] and Aifan Chen[a]

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029 China

[b] National Engineering Research Center for Rare Earth Materials, General Research Institute for Nonferrous Metals, and Grirem Advanced Materials Co. Ltd., Beijing 100088, China

[c] Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

*Corresponding author:
Tel.: + 86 010 64961040
E-mail: luorx@mail.buct.edu.cn

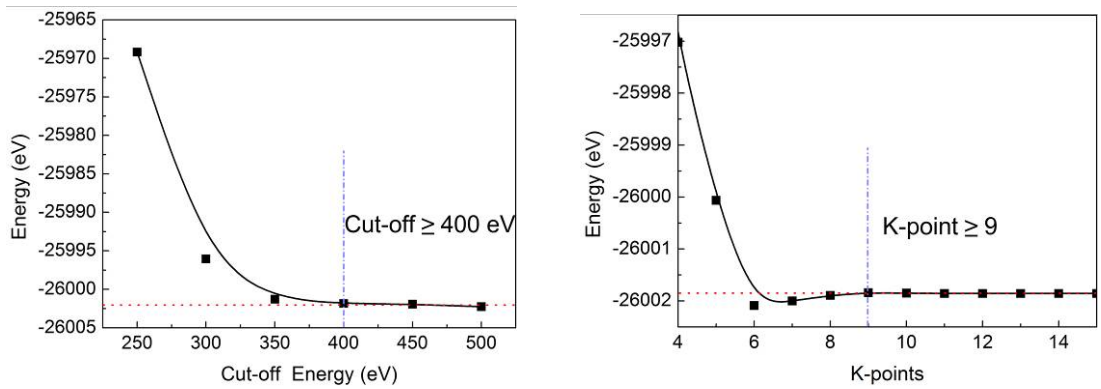

Fig. S1 Energy convergence of bulk WO_3 with increasing plane wave cut-off energy (left) and number of k-points (right).

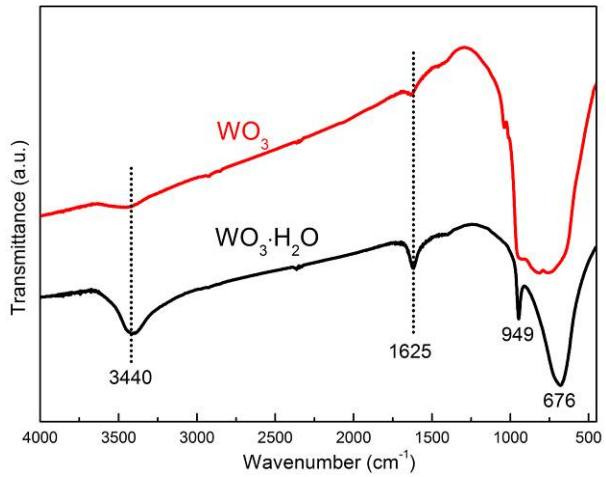

Fig. S2 FT-IR spectra of the $WO_3 \cdot H_2O$ and WO_3 samples.

Fig. S2 shows the FT-IR spectra of the $WO_3 \cdot H_2O$ and WO_3 samples. The FT-IR spectrum of as-synthesized $WO_3 \cdot H_2O$ shows a broad band in the range 3000-3700 cm^{-1}, which can be assigned as O-H stretching vibrations of the adsorbed water. The peaks located at 1625 cm^{-1} is indexed to O-H bending modes of the adsorbed water. Below 1000 cm^{-1}, the FT-IR spectrum shows a small and sharp peak at 949 cm^{-1}, assigned as the stretching of short W=O bonds of $WO_3 \cdot H_2O$. The broad band around 676 cm^{-1} is attributed to the stretching of O-W modes. The absence of carbonyl peak around 1730 cm^{-1} indicates removing of oxalate during the washing process. For the annealed WO_3 sample (red line), the hydrogen bonded W-OH groups show a large

decrease due to dehydration of $WO_3 \cdot H_2O$. The broad absorption peaks in the range 500–1000 cm^{-1} are characteristic of the different O-W-O stretching vibrations in the WO_3 crystal lattice.

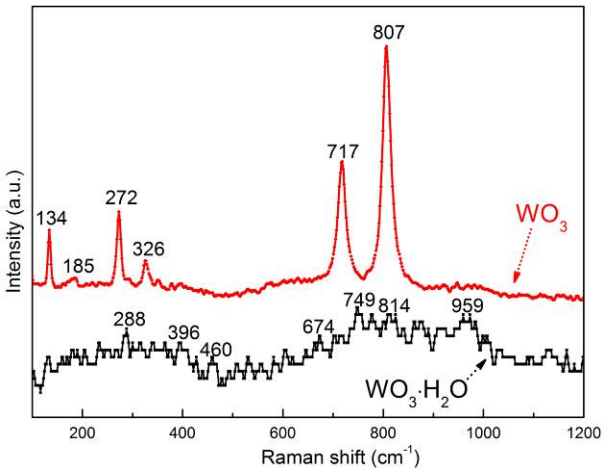

Fig. S3 Raman spectra of the $WO_3 \cdot H_2O$ and WO_3 samples.

The structural defects and disorders of the samples are further identified by Raman spectra, as shown in Fig. S3. For the $WO_3 \cdot H_2O$ sample, two characteristic Raman peaks of $WO_3 \cdot H_2O$ at 959 and 674 cm^{-1} are obsorved. The band situated at 959 cm^{-1} is attributed to the symmetric stretching mode of terminal (W=O) groups; this mode is common for all types of tungsten trioxide hydrates. The peak observed at 674 cm^{-1}, which can be attributed to stretching modes arising from $W\text{-}OH_2$, is consistent with the presence of $WO_3 \cdot H_2O$ phases. The weak transitions at 460 cm^{-1} may be associated with water librations. After annealing, the peaks at 959 and 674 cm^{-1} almost disappear, while six well-defined peaks arising from WO_3 phase (134, 185, 272, 326, 717 and 807 cm^{-1}) can be observed. This indicates that $WO_3 \cdot H_2O$ has completely transformed into monoclinic WO_3 after annealing, and the particle size and crystallinity increase. As is reported in the literatures, WO_3 consists of network of corner-sharing WO_6 octahedron units which are capable of forming clusters. The crystalline clusters are

supposed to be connected to each other by W-O-W. The peaks at 807 and 717 cm^{-1} are assigned as the stretching of W-O-W, in which the longer W-O-W bonds are responsible for the stretching mode at 717 cm^{-1} and the shorter W-O-W bonds are the source of the 807 cm^{-1} peak. The peaks at 272 and 326 cm^{-1} are assigned to the W-O-W bending vibrations of bridging oxygen, whereas those observed at 134 and 185 cm^{-1} belong to the lattice vibration of crystalline WO_3.

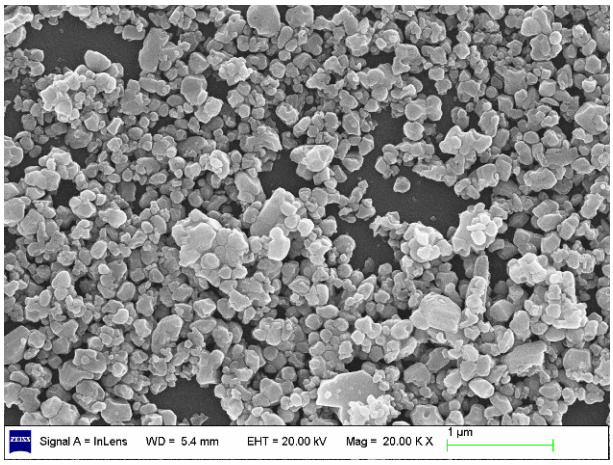

Fig. S4 FESEM micrograph of commercial WO_3 powder.

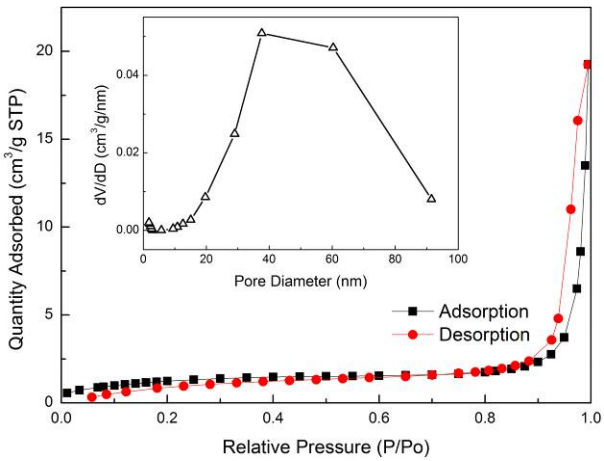

Fig. S5 N_2 adsorption-desorption isotherm and the corresponding pore size

distribution (inset) of commercial WO_3 particles.

The commercial WO_3 particles exhibit type-III pattern of isotherm with H4 hysteresis loop, in which the two branches are almost vertical and nearly parallel over an appreciable range of relative pressure. The BET surface area was determined to be 4.8 $m^2 \cdot g^{-1}$, comparatively lower than that of hierarchical WO_3 ca. 12.8 $m^2 \cdot g^{-1}$. The result is in accordance with the gas-sensing measurements.

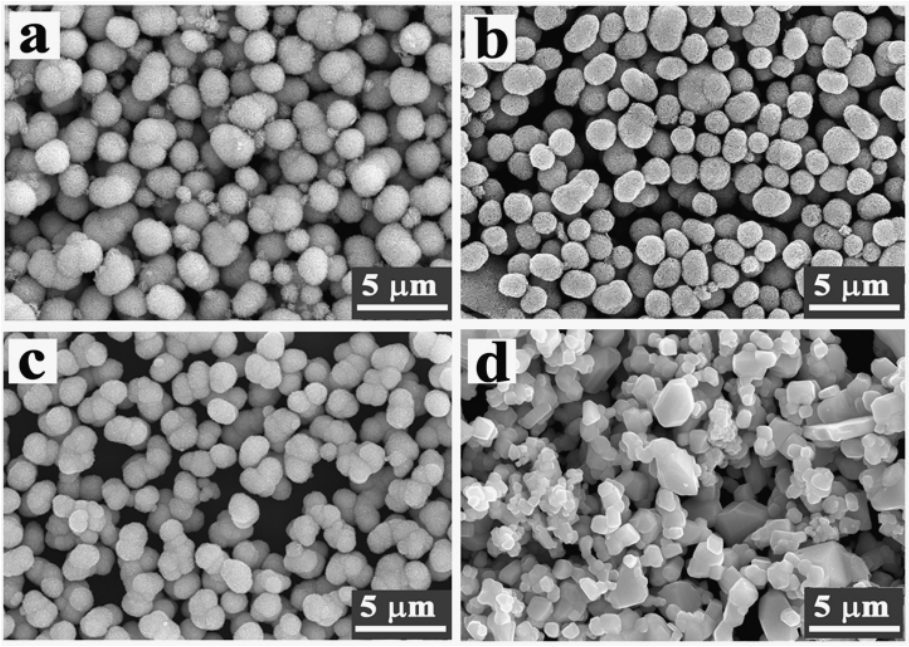

Fig. S6 FESEM micrographs of (a) as-synthesized hierarchical $WO_3 \cdot H_2O$ and anhydrous hierarchical WO_3 after annealing at (b) 500°C, (b) 700°C and (b) 900°C.

High annealing temperature, such as 900°C, would lead to breakage of the hierarchical morphology of WO_3. However, there would be no obvious change in morphology at low annealing temperatures, such as 500°C.