## Vertically aligned, double-sided, and self-supported $3D WO_3$

## nanocolumn bundles for low-temperature gas sensing

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## **Electronic Supplementary Information**



Fig. S1 SEM images of the samples annealed at 300 °C at different magnifications: panorama image (a), front image (b), and profile image (c). All the scale bars are 3 µm.



Fig. S2 XRD patterns of the samples annealed at 300 °C for 2 h (a) and the as-prepared WO<sub>3</sub> (b).



Eqn S1. The texture coefficient of (002) facets

Here,  $TC_{002}$  is the relative texture coefficient of the diffraction peaks of (002) over (200).  $I_{hkl}$  is the measured diffraction intensity of the (hkl) facet, and  $I_{hkl}^{0}$  is the corresponding value of the standard XRD patterns.



Fig. S3 ESEM images of the vertically aligned, double-sided, and self-supported 3D WO<sub>3</sub> nanocolumn bundles prepared by adding different amount of HCl: (a) 0 mL, (b) 0.5 mL, (c) 3 mL and (d) 6 mL in the solution. All the scale bars are 5  $\mu$ m.

To further demonstrate our assumption and comprehend the function of acid (HCl) directing morphology and slowing down the synthetic process, the elaborate experiments on increasing amount of acid are considered in the solution. (i) When the HCl is absent in the reaction system, lots of plates or bulk materials (see the red dashed circle in Fig.S3a<sup>†</sup>) are found. Following the hydrolysis of WCl<sub>6</sub> precursors with time increasing, according to the reaction formula (the process of the reactions can be described as follows: WCl<sub>6</sub> + nC<sub>2</sub>H<sub>5</sub>OH  $\rightarrow$  W(C<sub>2</sub>H<sub>5</sub>O)<sub>n</sub>Cl<sub>6-n</sub> + nHCl and WCl<sub>6</sub> + 4H<sub>2</sub>O  $\rightarrow$  WO<sub>3</sub>·H<sub>2</sub>O + 6HCl), small amount of HCl will be generated, as well as obtained similar self–supported 3D WO<sub>3</sub>which may infer that little HCl direct the morphology. (ii) When adding 0.5 mL HCl in the solution, the special microstructures of the intermediates are similar with the final morphology, while the thickness is thinner compared with the final products, as shown in Fig. S3b<sup>†</sup>. Considering the reaction is reciprocal, so that more HCl will slow down the reaction from WCl<sub>6</sub> to WO<sub>3</sub>, and the appropriate HCl (1.5 mL) will also direct the synthesized WO<sub>3</sub> transfer the plate-like structure into vertically aligned, double-sided, and column bundles (as shown in the Fig. 1a) with a certain thickness, which perfectly demonstrate our proposal. (iii) As the amount of HCl increase to 3 mL, the excess HCl will strongly deter the reaction from WCl<sub>6</sub> to WO<sub>3</sub> (see Fig. S3c<sup>†</sup>). The thickness of structure is thickened, the products may appear few amorphous nanoparticles (see green dashed circle in the SEM images). (iv) What's more, when the amount of HCl is up to 6 mL, so the final product will contain 3D self-supported WO<sub>3</sub> column bundles and amorphous primary nanoparticles at the same time, the morphology of the array structure is destroyed form the SEM images (see yellow dashed circle in Fig. S3d<sup>†</sup>). All mentioned above well demonstrate that HCl is a key to help directing the arrays with appropriate HCl. However, the detailed formation mechanism of this special structure needs to be further explored.



Fig. S4 (a) Response of the WO<sub>3</sub> at different annealed temperatures at optimum operating temperatures of 110  $^{\circ}$ C to 10 ppm NO<sub>2</sub>; (b) The SEM image of the sample annealed at 500  $^{\circ}$ C.

The higher annealed temperature like 400 °C and 500 °C have also been considered, the response of the  $WO_3$  sensor is shown in the Fig. S4a. The result reveals that the response increases firstly and then decreases with increasing the annealed temperature. The maximum responses of as-prepared, annealed @300 °C, annealed @400 °C, and annealed @500 °C toward 10 ppm NO<sub>2</sub> are 10, 20.5, and 15.3, and 7.1, respectively, at an optimum operating temperature of 110 °C. Owing to the morphology of the sample annealed at 500 °C is destroyed as can be seen from the image in Fig. S4b, which may be the key factor resulting in the response decrease.



Fig. S5 (a) Transient responses of WO<sub>3</sub> annealed at 300 °C to 100 ppb and 500 ppb NO<sub>2</sub> at 110 °C; (b) The response ( $t_{res}$ ) and recovery ( $t_{rec}$ ) time measured from the response-time data to 10 ppm NO<sub>2</sub> at optimum operating temperature of 110 °C.



Fig. S6 (a) Transient responses of WO<sub>3</sub> annealed at 300  $^{\circ}$ C to 100 ppm methanol, NH<sub>3</sub>, and ethanol gases at operating temperature of at 110  $^{\circ}$ C and 170  $^{\circ}$ C.

In order to give solid evidences to support the slight response of WO<sub>3</sub> towards 100 ppm methanol,  $NH_3$ , and ethanol gases attribute to the relatively low operating temperature of the gas sensor. We increase the operating temperature from 110 °C to170 °C to detect the interfering gases. The results found that their response increase with increasing the operating temperature (see the Fig. S6†), which interpreted the relatively low operating temperature of the gas sensors result in slight response to the interfering gases.



Fig. S7 Nitrogen adsorption-desorption isotherms of the 3D hierarchical WO3.

The nitrogen adsorption–desorption isotherms were measured to obtain the Brunauer-Emmett-Teller (BET) specific surface area of our 3D hierarchical WO<sub>3</sub>, as shown in Fig. S7<sup>†</sup>. The surface area of the sample annealed at 300 °C is evaluated to be 72.32 m<sup>2</sup>/g, indicating that the relative high surface area is one reason for the high response to detecting NO<sub>2</sub>, as well as the similar result is also reported by the Ji et al. (Ref. 34).

34. Q.-q. Jia, H.-m. Ji, D.-h. Wang, X. Bai, X.-h. Sun and Z.-g. Jin, J. Mater. Chem. A, 2014, 2, 13602-13611.