

## **Electronic Supplementary Information (ESI):**

### **Zinc oxide aerogel-like materials with an intriguing interwoven hollow-sphere morphology for selective ethanol sensing**

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**Materials:**

Zinc acetate dihydrate, hexamine, ethanol, commercial ZnO and gas sensing chemical reagents were purchased from Beijing Chemicals Company, China, D-glucose anhydrous was purchased from AMRESCO, yeast extract powder was from OXOID, lacto-peptone was purchased from Beijing Aoboxing Biotechnology Co, bacterial strain acetobacter xylinum HN001 was kindly provided by the School of Materials Science and Engineering, Tianjin University, China. Distilled water was used throughout without further purification.

**Preparation of BC aerogel and ZnO/BC containing 70 wt% of ZnO (ZnO/BC):**

BC aerogel and ZnO/BC were prepared according to the reported procedures.<sup>1</sup> BC aerogel of specified dimension was put into a reflux vessel containing 0.5 g of zinc acetate dihydrate and 30 mL of ethanol. Refluxing took place at 80 °C for 5 h. It was then transferred to a PTFE-lined stainless steel autoclave containing 20 mL of ethanol and 0.2 g of hexamine. The ZnO/BC nanocomposite foam containing 70 wt% of ZnO was obtained after 6 h at 85 °C under autogenous pressure conditions, isolated from the reaction mixture and solvent-exchanged three times using tertiary butanol. ZnO/BC was recovered from the organogel by freeze drying as white foams.

**Preparation of ZnO aerogels-like materials:**

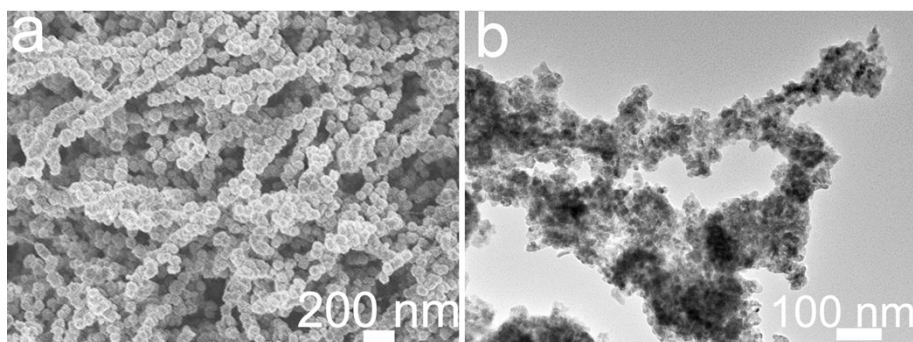
ZnO aerogel was obtained by heating ZnO/BC at a heating rate of 2 °C min<sup>-1</sup> in air from room-temperature to 450 °C and 550 °C for 5 h, and to 650 °C and 750 °C for 3 h. To study the effect of heating rate on the morphology of end products, ZnO/BC was heated at a heating rate of 8 °C min<sup>-1</sup> at 450 °C and 550 °C for 5 h. The density of ZnO-550 is calculated to be about 0.18 g cm<sup>-3</sup>.

**Characterization:**

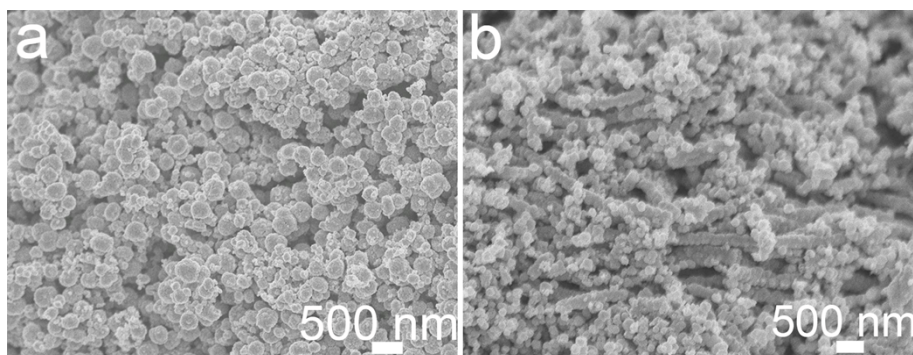
Rigaku D/Max 2550 X-ray diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was employed to determine the crystal phase of the samples. The morphology of the samples was characterized by scanning electron microscope (SEM, JEOL JSM 6700F). Transmission electron microscope (TEM), high-resolution transmission electron microscope and selected area electron diffraction (SAED) were determined by FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV. XPS spectra were recorded on an ESCALAB 250 X-ray photoelectron spectrometer, using a monochromatic X-ray source (Al K $\alpha$   $h\nu = 1486.6 \text{ eV}$ ). The FT-IR spectra were recorded on a Bruker IFS 66v/S FTIR spectrometer. The thermogravimetric (TG) analysis was carried out on NETZSCH STA 449C TG thermal analyzer. Nitrogen absorption and desorption isotherms was performed on Micromeritics ASAP 2020M system.

**Gas sensing measurement:**

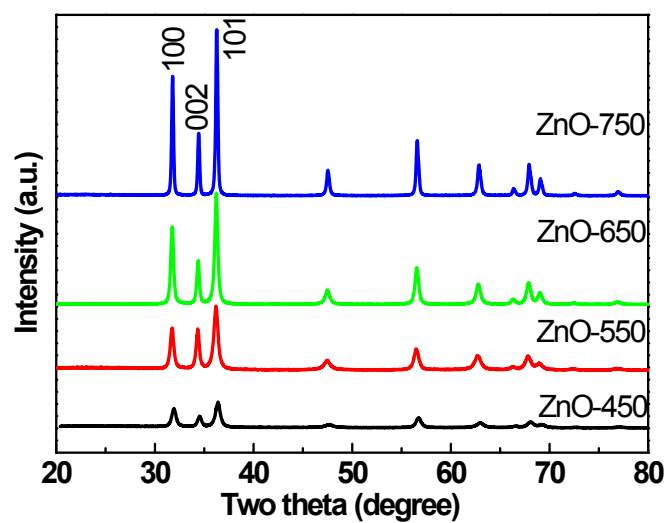
Gas sensing devices were fabricated based on reported procedures.<sup>2</sup> Grinded ZnO materials were dispersed in water forming viscous slurry, which was then coated onto a Al<sub>2</sub>O<sub>3</sub> ceramic tube with a pair of Au electrode and four Pt wire. Next, a Ni-Cr electric resistance wire was inserted into the ceramic tube. The air-dried ZnO-dispersed sensor was aged at about 300 °C for 3-7 days to form a conducting layer with the working area of 1 mm $\times$ 4 mm. Gas sensing tests were performed on a commercial CGS-8 Gas Sensing Measurement System (Beijing Elite Technology Co Ltd, China). Target gases were introduced into test chamber with a micro-syringe. Sensing measurements were conducted at 300 °C (heating current of 150 mA) in a 1 L static gas distribution system where ethanol concentration was set at 5, 20, 50, 100, 200, 500 and 1000 ppm. The same procedures were applied to the sensing measurements of reference samples (ZnO-650, ZnO-750 and a commercial ZnO, termed as ZnO-coml). Gas sensing tests were conducted using a series of other gases such as methanol, ethane, formaldehyde, benzene, ethylene, acetaldehyde and methylbenzene for selectivity studies. The sensor sensitivity ( $S$ ) is defined as  $S = R_a/R_g$ , where  $R_a$  and  $R_g$  are the electrical resistances of the sensor in air and in test gas, respectively.<sup>2</sup>



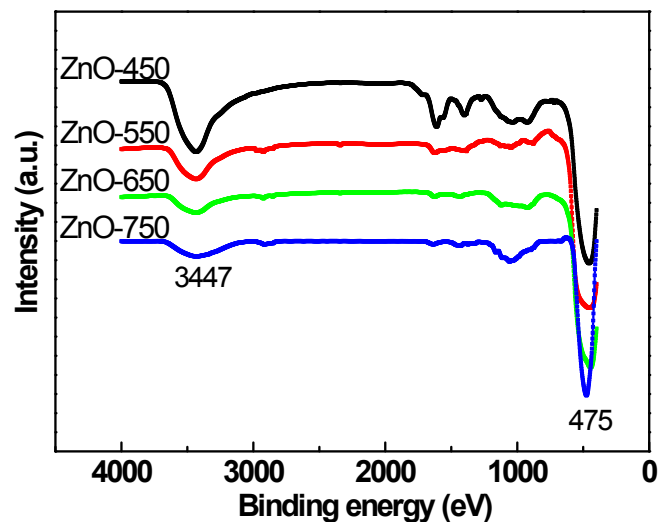
**Fig. S1** (a) SEM image of ZnO/BC showing the string-beaded morphology, (b) TEM image of ZnO/BC showing the aggregated ZnO nanocrystals with approximate dimensions of 20 nm.



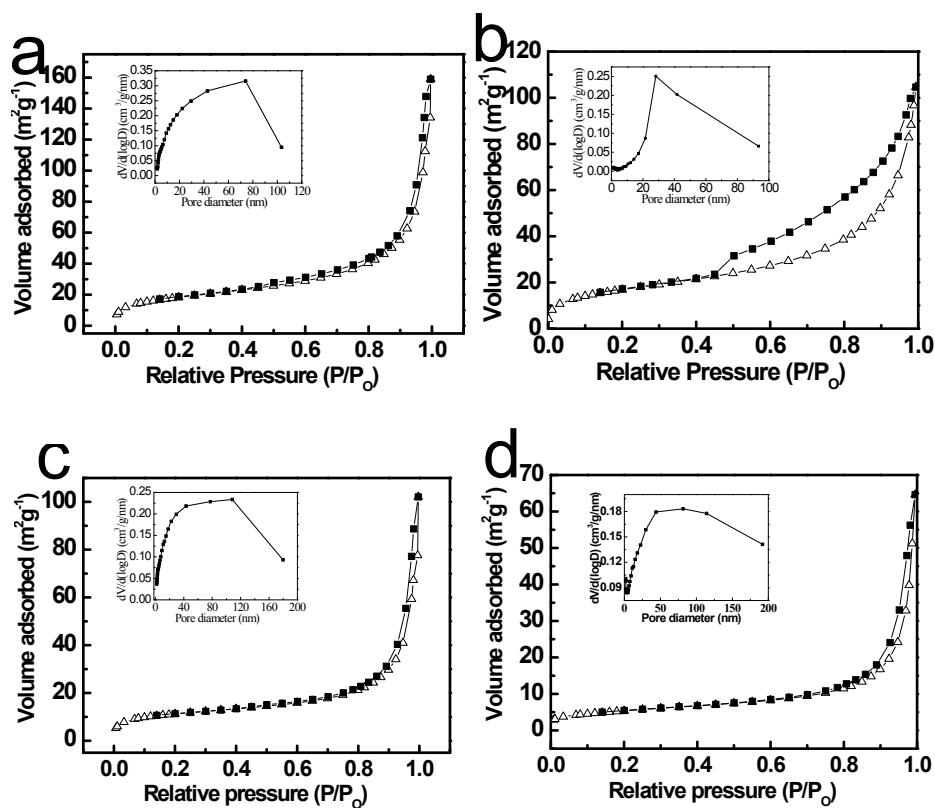
**Fig. S2** SEM images of ZnO obtained by calcining ZnO/BC at  $8\text{ }^{\circ}\text{C min}^{-1}$  to: (a)  $450\text{ }^{\circ}\text{C}$  for 5 h where the monolithic architecture no longer retains, and (b)  $550\text{ }^{\circ}\text{C}$  for 5 h where the monolithic architecture partially lost.

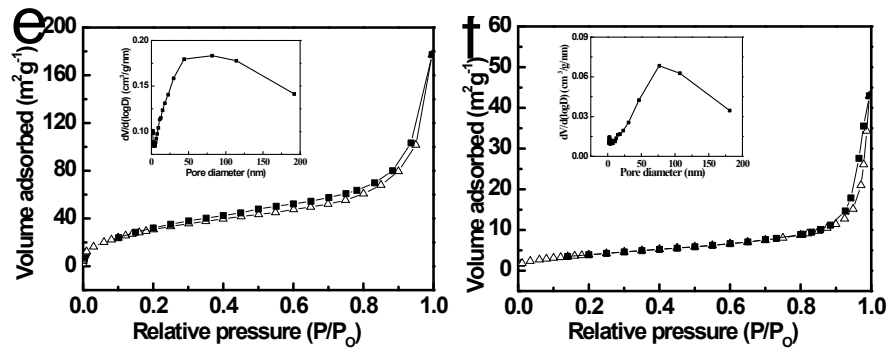


**Fig. S3** XRD patterns of ZnO-450, ZnO-550, ZnO-650 and ZnO-750, showing that wurtzite ZnO phase is the only crystalline phase and the crystallinity of ZnO increases with increasing calcination temperatures.

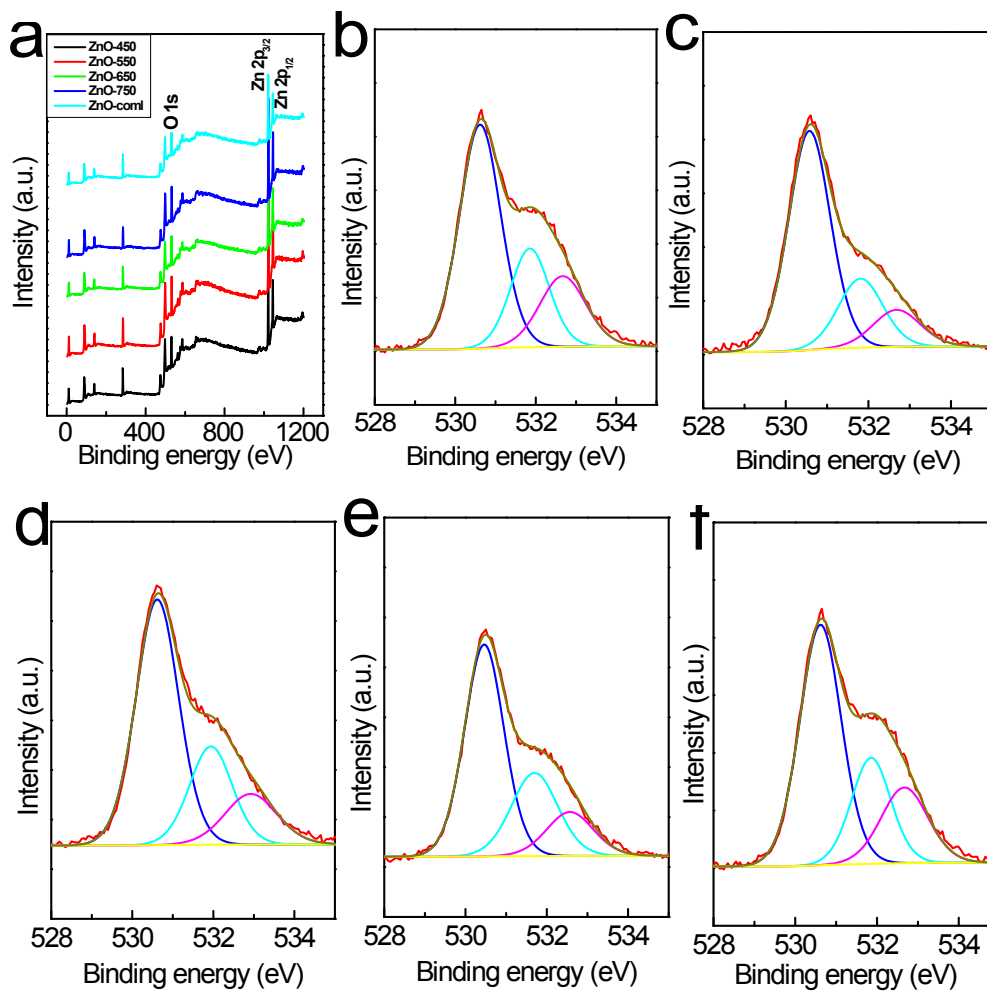


**Fig. S4** IR spectra of ZnO-450, ZnO-550, ZnO-650 and ZnO-750. The absorption peaks centered at 3447  $\text{cm}^{-1}$  and 475  $\text{cm}^{-1}$  are attributed to the stretching vibrations of O-H and the Zn-O, respectively.

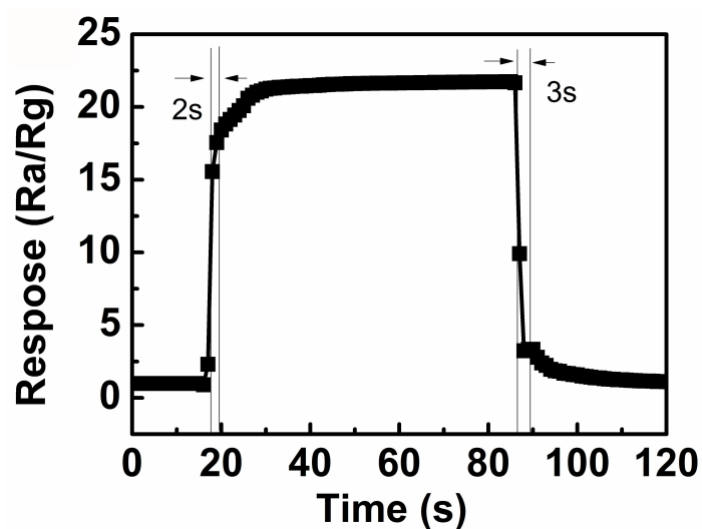




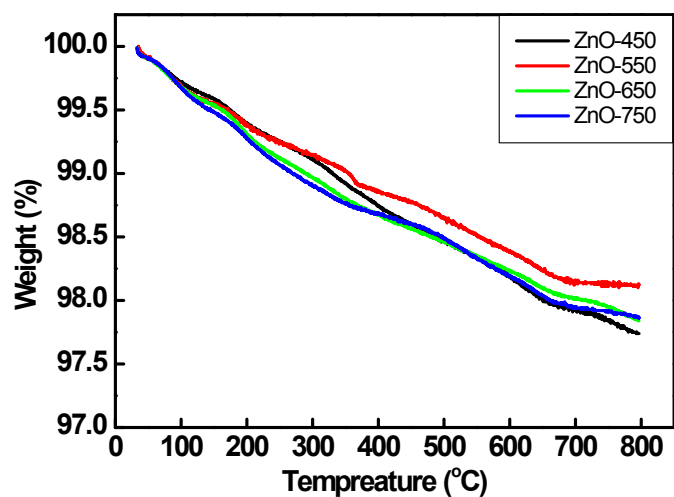
**Fig. S5** Nitrogen adsorption-desorption isotherms with pore size distributions based on the BJH model (Inset): (a) ZnO-450, (b) ZnO-550 (c) ZnO-650, (d) ZnO-750, (e) ZnO/BC and (f) ZnO-coml.



**Fig. S6** (a) Survey XPS spectra. The deconvoluted XPS peak of O1s: (b) ZnO-450, (c) ZnO-550, (d) ZnO-650, (e) ZnO-750 and (f) ZnO-coml.



**Fig. S7** The response and recovery characteristic of the ZnO-550 sensor for 100 ppm of ethanol at 300 °C.



**Fig. S8** The TG analysis of ZnO-450, ZnO-550, ZnO-650 and ZnO-750 in air.

**Table S1.** Comparing the ethanol sensing properties of selected ZnO sensors with the ZnO-550 sensor of the current work.

	Synthesis route	Sensing temperature (°C)	Sensitivity* ( $R_a/R_g$ )	Response/ Recovery time (s)	References
1	Hydrothermal	332	8	10, 30	<a href="#">Sens. Actuators B Chem., 2006, 113, 526</a>
2	Hydrothermal	350	10	10, 20	<a href="#">Sens. Actuators B Chem., 2007, 126, 604</a>
3	Microwave	380	5	32, 17	<a href="#">Adv. Mater., 2008, 20, 4547</a>
4	Electrospinning	270	10	3, 5	<a href="#">J. Phys. Chem. C 2009, 113, 19397</a>

5	Hydrothermal	280	3	No data	<a href="#">Cryst. Growth Des., 2009, 9, 3532</a>
6	Hydrothermal	300	5.8	10, No data	<a href="#">J. Mater. Chem., 2011, 21, 349</a>
7	Sol-gel	300	4	40, 60	<a href="#">Sens. Actuators B Chem., 2011, 1, 73</a>
8	Hydrothermal	320	25	60, 50	<a href="#">Sens. Actuators B Chem., 2012, 162, 237</a>
9	Hydrothermal	220	5	No data	<a href="#">CrystEngComm, 2012, 14, 1775</a>
10	High-temperature gas phase reaction	140	1.9	No data	<a href="#">Adv. Mater. 2012, 24, 543</a>
11	Reflux/Hydrothermal assembly Controlled calcination	300	22	2, 3	Current work

\*: The ethanol sensing performance of above sensors were evaluated for 100 ppm of ethanol.

### ESI References

1. P. P. Wang, J. Zhao, R. F. Xuan, Y. Wang, C. Zou, Z. Zhang, Y. Wang and Y. Xu, *Dalton Trans.*, 2014, **43**, 6762-6768.
2. Q. Qi, T. Zhang, L. Liu, X. J. Zheng, Q. J. Yu, Y. Zeng, H. B. Yang, *Sens. Actuators B Chem.*, 2008, **134**, 166-170.