

Electronic Supporting Information

Three-dimensional hierarchical Co₃O₄ nano/micro-architecture: synthesis and ethanol sensing properties

Tie Liu,^a Jingyuan Liu,^{a,*} Qi Liu,^a Yanbo Sun,^{b,*} Xiaoyan Jing,^a Hongquan Zhang,^c and Jun Wang^a

^a Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin, 150001, PR China.

^b State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University Changchun, 130023, PR China.

^c School of Automation, Harbin Engineering University, 150001, PR China.

* Corresponding author: Tel.: +86 451 8253 3026; Fax: +86 451 8253 3026; E-mail: zhqw1888@sohu.com.

Experimental procedure

Synthesis of Co₃O₄ cubes and nanoparticles. In typical synthesis procedure, 1mmol Co(NO₃)₂·6H₂O and some NaCl were completely dissolved in ethylene-glycol (65ml) to form a transparent solution. Brief, 4 mmol NH₄F were added to solution above and dissolved completely. After ultrasonic and stirred treatments, the final solution was transferred to a Teflon-lined stainless autoclave, which was heated 180°C for 8h in air flow electric oven. After cooling down, the product was washed by distilled water and ethanol several times prior to being dried at 60°C for 10h. Finally, the final cubic sample was collected after the calcination process at 500°C for the gas sensing test further. Those nanoparticles were prepared by the similar process above just changing the solvent (only 70mL ethanol) and the alkaline source (urea).

Table. S1 Gas responses to ethanol of the sensors in the recent study and those reported in the literature.

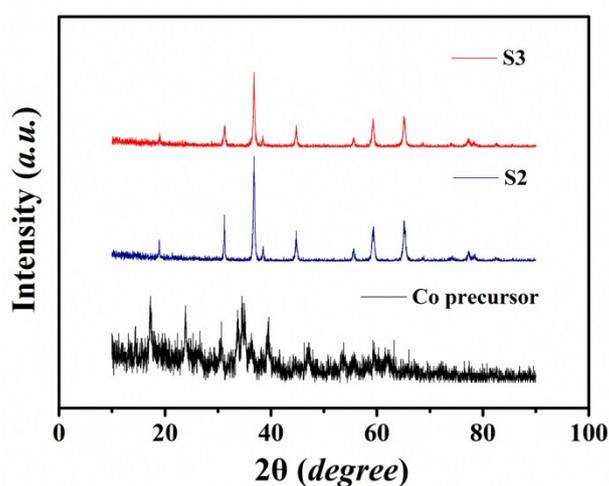
Materials	Structure	Ethanol conc.(ppm)	T (°C)	Sensitivity	Reference
ZnO/Co ₃ O ₄	pyramidal-like	500	400	~10	S1
α -Fe ₂ O ₃	Yolk-shell	100	240	~13	S2
SnO ₂ / α -Fe ₂ O ₃	Hollow spheres	10	250	~15	S3
ZnO	Brush-like	50	265	~10	S4
Co-doped ZnO	nanowires	5	450	~5	S5
Zn-doped SnO ₂	Sphere-like	100	213	~14.4	S6
ZnO	Hollow spheres	50	420	~8.5	S7
NiO/SnO ₂	Nanofibers	100	330	~3.5	S8
ZnFe ₂ O ₄	nanoparticles	100	200	~6	S9
Co ₃ O ₄	Lamellar cubes	50	170	~5.1	This work
Co ₃ O ₄	Needle-shaped	50	170	~13.4	This work

Conc., concentration; T, the optimal working temperature

Table. S2 ICP-MS analysis data of S1 before/after sensing reaction.

Elements No.	Co	
	Before (c ₁)	After (c ₂)
1	11.27	11.26
2	11.20	11.22
3	11.23	11.23
Average	11.33	11.37
$\Delta Con. (c_2 - c_1)$	+0.04	

Con., ppm level

**Fig. S1** XRD patterns of precursor of S1, Co₃O₄ cubes (S2) and Co₃O₄ nanoparticles (S3).

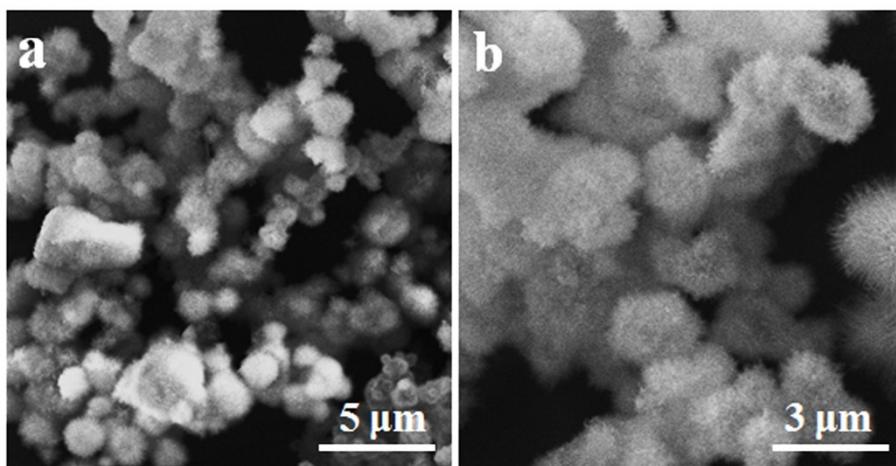


Fig. S2 The SEM images of S1 at different magnifications.

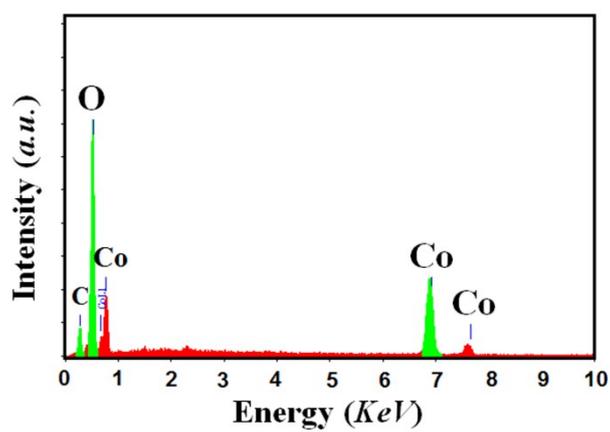


Fig. S3 The EDS analysis spectrums of Co_3O_4 needle-shaped microspheres (S1).

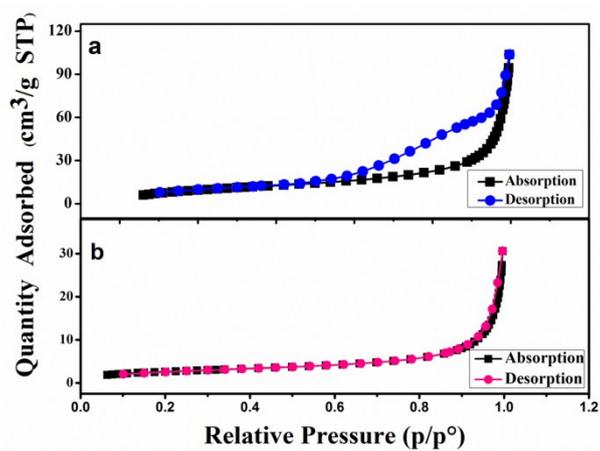


Fig. S4 The BET data of control groups: (a) S2 and (b) S3.

References:

- S1. D. Bekermann, A. Gasparotto, D. Barreca, C. Maccato, E. Comini, C. Sada, G. Sberveglieri, A. Devi and R. A. Fischer, *ACS applied materials & interfaces*, 2012, **4**, 928-934.
- S2. L. Wang, Z. Lou, J. Deng, R. Zhang and T. Zhang, *ACS applied materials & interfaces*, 2015, **7**, 13098-13104.
- S3. P. Sun, X. Zhou, C. Wang, K. Shimano, G. Lu and N. Yamazoe, *J. Mater. Chem. A*, 2014, **2**, 1302-1308.
- S4. Yuan Zhang, Jiaqiang Xu, Qun Xiang, Hui Li, Qingyi Pan, and Pengcheng Xu, *J. Phys. Chem. C*, 2009, **113**, 3430 - 3435.
- S5. H. S. Woo, C. H. Kwak, J. H. Chung and J. H. Lee, *ACS applied materials & interfaces*, 2014, **6**, 22553-22560.
- S6. Y. Guan, D. Wang, X. Zhou, P. Sun, H. Wang, J. Ma and G. Lu, *Sensors and Actuators B: Chemical*, 2014, **191**, 45-52.
- S7. Y. Tian, J. Li, H. Xiong and J. Dai, *Appl. Surf. Sci.*, 2012, **258**, 8431-8438.
- S8. L. Liu, Y. Zhang, G. Wang, S. Li, L. Wang, Y. Han, X. Jiang and A. Wei, *Sensors and Actuators B: Chemical*, 2011, **160**, 448-454.
- S9. J.-M. S. Jie Zhang, He-Lin Niu, Chang-Jie Mao, Sheng-Yi Zhang, Yu-Hua Shen, *Sensors and Actuators B: Chemical*, 2015, **221** 55-62.