Porous ZnO/$ZnCo_2O_4$ Hollow Spheres: Synthesis, Characterization, and Their Applications in Gas Sensors

Xin Zhou[a], Wei Fenga, Chen Wang[a], Xiaolong Hu[a], Xiaowei Li[a], Peng Sun[a]*, Kengo Shimanoe[b], Noboru Yamazoe[b], Geyu Lu[a]*

a State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, People's Republic of China.

b Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816-8580, Japan.

**Corresponding Authors: Tel: +86 431 85167808; Fax: +86 431 85167808 E-mail addresses: spmaster2008@163.com, lugy@jlu.edu.cn*

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by a facile precipitation route according to the literature with some modifications[1]. All of the reactants were analytical grade and directly used without any further purification. In a typical process, $ZnSO_4$ aqueous solution （100mL, 1.5 mol L^{-1}）was added dropwise into NH_4HCO_3 solution (200mL, 1.26mol L^{-1}) at 40 °C. After aged for 1 h, the precipitate was dried and collected. Finally, the precipitate was annealed at 800°C under air atmosphere for 30 min (the same calcinations condition with ZnCo-glycolate precursor) to obtain ZnO nanoparticles.

Synthesis of $ZnCo_2O_4$ nanoparticles

In order to get $ZnCo_2O_4$ nanoparticles, the as-obtained $ZnO/ZnCo_2O_4$ composites were immersed in 2M NaOH aqueous solution and dispersed, and then the solution was maintained at room temperature for 30 min under ultrasonication. Finally, the products were centrifuged, dried and collected.

Preparation of $ZnO/ZnCo_2O_4$ nanoparticles

The as-obtained porous $ZnO/ZnCo_2O_4$ hollow spheres were ball milled for 10 minutes to prepare $ZnO/ZnCo_2O_4$ nanoparticles

Preparation of the mixture of ZnO and $ZnCo_2O_4$

The as-prepared ZnO and $ZnCo_2O_4$ nanoparticles were ball milled with a molar ratio of 1:1 to obtain the simple mixture of ZnO and $ZnCo_2O_4$.

1 N. Han, X. F. Wu, L. Y. Chai, H. D. Liu, Y. F.Chen, *Sens. Actuators B,* 2010, 150, 230-238.

Low-magnification FESEM images of nanoparticles: (a) $ZnO/ZnCo_2O_4$ (b) ZnO, (c) $ZnCo_2O_4$.

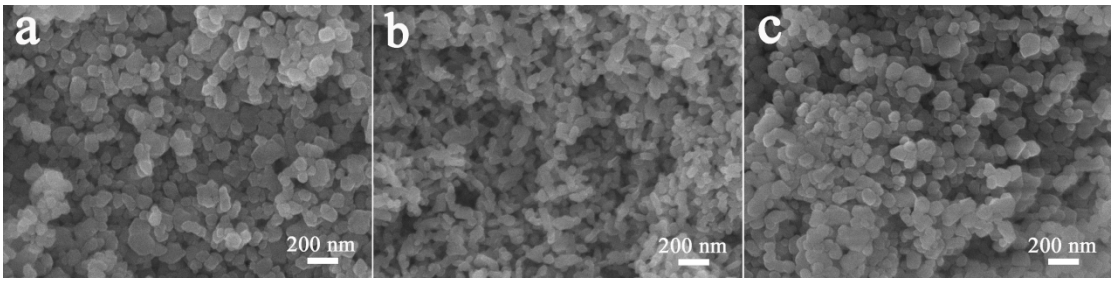

Fig. S1† Low-magnification FESEM images of nanoparticles: (a) $ZnO/ZnCo_2O_4$, (b) ZnO, (c) $ZnCo_2O_4$.

XRD pattern of the ZnO products.

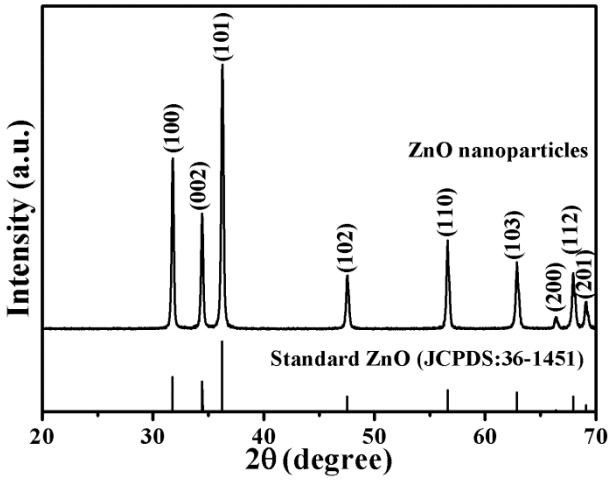

Fig. S2† XRD pattern of the ZnO products.

XRD pattern of the $ZnCo_2O_4$ nanoparticles

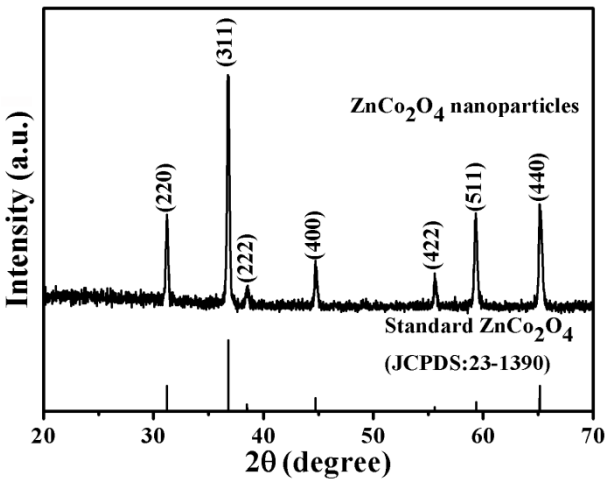

Fig. S3† XRD pattern of the $ZnCo_2O_4$ nanoparticles

XRD pattern of the ZnCo-glycolate precursor

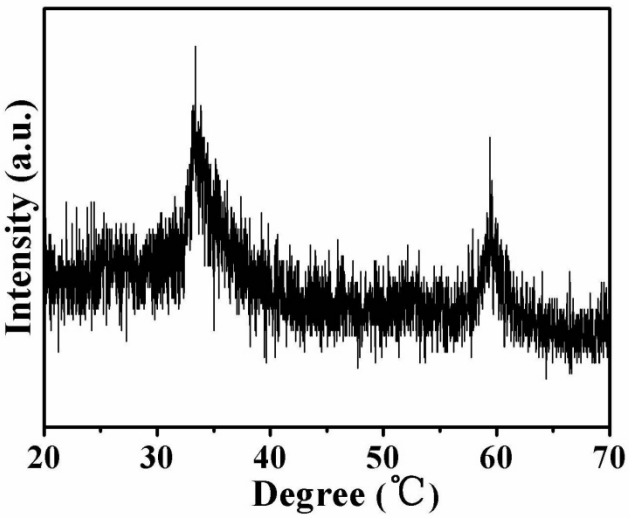

Fig. S4† XRD pattern of the ZnCo-glycolate precursor.

TEM images of the precursors obtained after solvothermal treatment for (a) 3h, (b) 6h, (c) 9h

and (d) 12h.

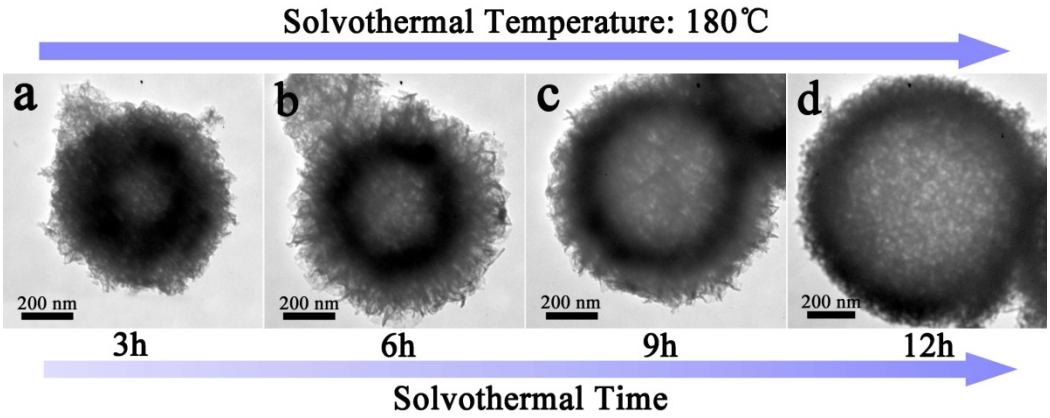

Fig. S5† TEM images of the precursors obtained after solvothermal treatment for (a) 3h, (b) 6h, (c) 9h and (d) 12h.

Displaying five periods of response-recovery curve

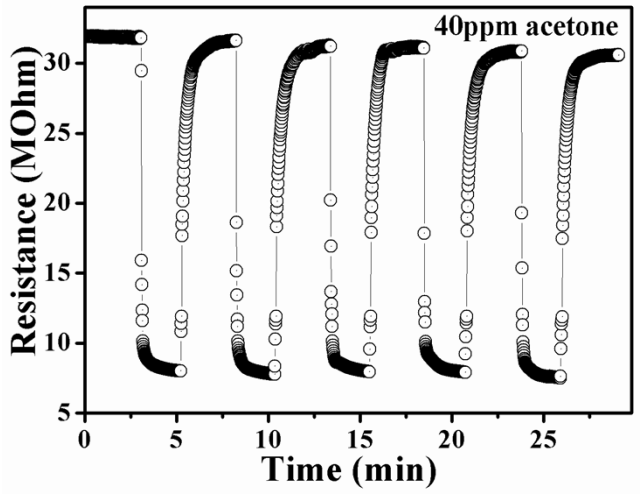

Fig. S6† Displaying five periods of response-recovery curve.

Pore-size distribution plot of $ZnO/ZnCo_2O_4$ hollow spheres.

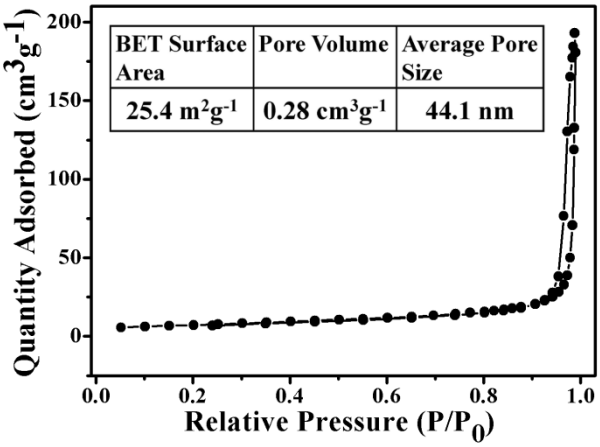

Fig. S7† Pore-size distribution plot of $ZnO/ZnCo_2O_4$ hollow spheres.