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Supporting Information

A CuO-ZnO Nanostructured p-n Junction Sensor for Enhanced n-butanol Detection

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Section S1:



Fig.S1. XRD patterns of Zn₅(CO₃)₂(OH)₆ precipitate obtained at 140 °C for 1 h and 12 h, respectively.



Fig. S2. SEM images of (a) Zn₅(CO₃)₂(OH)₆ precipitate obtained at 140 °C for 12 h and (b) Zn₅(CO₃)₂(OH)₆ precipitate obtained at 140 °C for 1 h.



Fig. S3. XRD patterns of Zn₅(CO₃)₂(OH)₆ precipitate obtained at 120 °C for 2 h, 4 h and 8 h, respectively.



Fig. S4. (a) TEM images of crystal nuclei in precursor solution and SEM images of Zn₅(CO₃)₂(OH)₆ precipitate obtained at 120 °C for (b) 2 h, (c) 4 h, (d) 12 h.



Fig. S5. Schematic of growth mechanism of the ZnO 2-D porous nanosheets.

As shown in Fig S1., the XRD pattern of precipitate obtained at 140 °C for 1 h (denoted as ZnCH-140-1) is well indexed with $Zn_5(CO_3)_2(OH)_6$ standard card (JCPDS No. 19-1458). Whereas, compared with that of the sample obtained at 140 °C for 12 h (denoted as ZnCH-140-12), the diffraction peaks of ZnCH-140-1 are broader and have lower intensity. This result suggests that the growth of Zn₅(CO₃)₂(OH)₆ was undergoing a Ostwald ripening process¹. However, as displayed in Fig S2., the morphology of ZnCH-140-1 and ZnCH-140-12 is similar. This indicates the Zn₅(CO₃)₂(OH)₆ microspheres formed rapidly at 140 °C. It is known that lower reaction temperature would slow down the growth of crystal and the formation of nanostructures^{2, 3}. Thus, the hydrothermal experiment was performed at 120 °C with different durations (2 h, 4 h and 8 h). The samples obtained at 120 °C for 2 h, 4 h and 8 h (denoted as ZnCH-120-2, ZnCH-120-4 and ZnCH-120-8) have been characterized using XRD (Fig. S3.) and SEM (Fig. S4.). As shown in Fig.S3, the XRD patterns show an increased crystallinity of the samples. This indicates an Ostwald ripening and grain growth process of the precipitate. Fig. S4. displays the morphology evolution from nuclei in precursor solution to samples after hydrothermal treating. The TEM image (Fig. S4.a) shows that the crystal nuclei are in the size of dozens of nanometer. After reaction for 2 hours, there are many incomplete microspheres for sample ZnCH-120-2. With time proceeding, the amount of the incomplete microspheres decreases. When the reaction time is 8 h, almost all of the incomplete microspheres are disappeared. Based on these results, the schematic illustration is shown in Fig. S5.. After adding NaCO₃, crystal nuclei were formed in the precursor solution. Via the hydrothermal treatment, $Zn_5(CO_3)_2(OH)_6$ nanosheets were formed rapidly and assembled on one center induced by L- glutamine and some microspheres were formed. Then, during the rest reaction time, the samples underwent an Ostwald ripening and grain growth process, and more microspheres were formed.



Fig.S6. XRD pattern of ZnO decorated with amorphous Cu-precipitate.



Fig.S7. (a) SEM image and (b) EDS analysis of ZnO with amorphous Cu-precipitate.

The growth mechanism of CuO-ZnO composite is also studied here. Firstly, the precipitate is obtained after mixing ZnO with Cu(NO₃)₂ solution and stirring for 0.5 h. The color of as-obtained precipitate is light blue. Its XRD pattern is shown in Fig.S6., which displays the characteristic of wurtzite ZnO. No other peak of impurities is observed. As shown in Fig.S7.a, there are many tiny precipitate nanoparticles on ZnO nanosheets. The EDS analysis shown in Fig.S7.b reveals that it is primarily composed of Zn, O and Cu elements. These results indicate the tiny nanoparticles could be assigned to amorphous Cu-precipitate. Besides, the Cu(NO₃)₂ solution has a low pH value. Thus, the surface of ZnO would be etched leading to an increasing pH value of the solution^{4, 5}. Then, Cu(OH)₂ might be formed around ZnO and adhered on it⁶. Thus, it is reasonable to preclude the amorphous Cu-precipitate to Cu(OH)₂. Under the hydrothermal process, the formation of CuO was due to dehydration and recrystallization of the Cu(OH)₂ as follow: ⁶

$$Cu(OH)_2(s) + 2OH(aq) \rightarrow Cu(OH)_4^2(aq) \rightarrow CuO(s) + 2OH(aq) + H_2O$$

As the growth continues, the CuO nanoparticles attach to each other following the oriented attachment with low-angle grain boundaries⁷. The porous and rough surface of ZnO nanosheets would serve to nucleate the CuO⁸. Thus, the CuO-ZnO composite p-n junction was formed.

Section S2:



Fig. S8. XPS spectra of (a) Zn 2p spectra of ZnO and CuO-ZnO, (b) Cu 2p spectrum of CuO-ZnO, O 1s spectra of (c) ZnO and (d) CuO-ZnO.

Samples	Zn 2p _{3/2}	O _L (Zn-O)	O _V (vacancy)	O _C (chemisorbed)
ZnO				
Binding energy (eV)	1021.3	530.2	531.9	532.8
Relative percentage (%)		69.7	17.6	12.7
CuO-ZnO				
Binding energy (eV)	1021.3	530.1	531.5	532.5
Relative percentage (%)		68.1	13.6	18.3

Table S1. Results of XPS spectra for ZnO and CuO-ZnO.

Section S3:



Fig. S9. SEM images of the films of (a) ZnO and (b) CuO-ZnO for Hall measurement.

Section S4:



Fig. S10. Nitrogen adsorption–desorption isotherms of (a) ZnO porous microsphere and (b) CuO-ZnO composite.

Section S5:



Fig. S11. Energy band structure of CuO-ZnO heterojunction in air.

Section S6:





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