Laser irradiation-induced Au-ZnO nanospheres with enhanced sensitivity and stability in ethanol sensing

Authors: Hao Zhang, Shouliang Wu, Jun Liu, Yunyu Cai, Changhao Liang, Changhao Liang

Date: 2017-10-31T00:00:00+00:00

Abstract

Incorporating noble metal nanoparticles on the surface or inner side of semiconductors to form a hybrid nanostructure is an effective route to improve the gas sensing performance of these semiconductors. In this study, we present novel Au-decorated ZnO nanospheres (Au-ZnO NSs) obtained by laser irradiation of liquids. Structural characterization indicated that the Au-ZnO NSs consisted of single crystalline ZnO NSs with few Au nanoparticles decorated on their surfaces and abundant encapsulated Au nanoparticles with relatively small sizes. Laser irradiation-induced heating-melting-evaporating processes are responsible for the formation of unique Au-ZnO NSs. Gas sensing properties of the Au-ZnO NSs, as gas sensing materials, were investigated and compared with those of pure ZnO NSs. The former showed lower working temperature, higher sensitivity, better selectivity, and good reproducibility. The response values of Au-ZnO NSs and pure ZnO NSs sensors to ethanol of 100 ppm were 252 and 75 at working temperature of 320 °C and 360 °C, respectively. The significant enhancements in gas sensing performance should be attributed to the electronic sensitization induced by the depleted layers between encapsulated Au nanoparticles and ZnO and chemical sensitization originating from the catalytic effects of Au nanoparticles decorated on the surfaces that dissociated molecular oxygen.

Full Text

Preamble

Laser irradiation-induced Au-ZnO nanospheres with enhanced sensitivity and stability in ethanol sensing

Hao Zhang,^a,b Shouliang Wu,^a Jun Liu,^a Yunyu Cai^a and Changhao Liang^*a,b

^a Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China. E-mail: chliang@issp.ac.cn

^b Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, 230026, China

Abstract

Incorporating noble metal nanoparticles on the surface or within semiconductors to form hybrid nanostructures represents an effective strategy for improving the gas sensing performance of these materials. In this study, we present novel Au-decorated ZnO nanospheres (Au-ZnO NSs) synthesized via laser irradiation of liquids. Structural characterization revealed that the Au-ZnO NSs consisted of single-crystalline ZnO nanospheres with a few Au nanoparticles decorated on their surfaces and numerous encapsulated Au nanoparticles of relatively small size. Laser irradiation-induced heating–melting–evaporation processes are responsible for the formation of these unique Au-ZnO NSs. The gas sensing properties of the Au-ZnO NSs were investigated and compared with those of pure ZnO NSs. The Au-ZnO NSs exhibited lower operating temperature, higher sensitivity, better selectivity, and good reproducibility. The response values of Au-ZnO NSs and pure ZnO NSs sensors to 100 ppm ethanol were 252 and 75 at operating temperatures of 320 °C and 360 °C, respectively. The significant enhancement in gas sensing performance can be attributed to electronic sensitization induced by the depletion layers between encapsulated Au nanoparticles and ZnO, as well as chemical sensitization originating from the catalytic effects of Au nanoparticles decorated on the surfaces that dissociate molecular oxygen.

Introduction

Gas sensors have attracted considerable attention for detecting and monitoring flammable, explosive, or toxic gases due to increasing concerns over the health and safety impacts of worsening gas pollution. Among various gas sensors, metal oxide semiconductor (MOS) sensors are widely investigated because of their low cost and easy maintenance. Since Seiyama et al. initially proposed the principle of gas sensing in 1962, numerous MOS materials have been explored as gas sensors. Examples of n-type metal oxides include ZnO, Fe O , In O , TiO , and WO , while p-type metal oxides include CuO, NiO, Co O , and Cr O . Among candidate gas sensor nanomaterials, ZnO has been extensively studied due to its high conductivity, good stability, and biocompatibility. However, several drawbacks, such as high operating temperature, low sensitivity, and poor selectivity, still limit the application of bulk ZnO as a gas sensor.

Numerous studies have been conducted to improve the gas sensing performance of ZnO by designing different nanostructures with large surface areas to increase active sites, such as nanocactus, porous nanoflakes, and flower-like structures.

Combining noble metal nanoparticles (NPs) (i.e., Au, Ag, or Pt) with ZnO to form hybrid nanostructures represents another efficient strategy for achieving desirable sensing performance. Two types of noble metal NP-ZnO hybrid nanostructures are currently employed: surface-modified and encapsulated configurations, both generally designed to improve sensing performance. The gas sensing performance of sensors can be enhanced by surface modification due to the catalytic effects of noble metal NPs in the dissociation of molecular oxygen (chemical sensitization) and electronic interaction leading to the formation of Schottky junctions between noble metal NPs and ZnO (electronic sensitization). However, this approach is limited by several issues. Coagulation and chemical poisoning of noble metal NPs occur at high working temperatures, resulting in the loss of catalytic activity. By contrast, encapsulated noble metal NPs are more stable than surface-decorated ones due to the protective ZnO shell. Moreover, the areas of Schottky junctions in encapsulated NPs are larger than those in surface-modified NPs because of the complete surface contact between Au and the ZnO shell. However, the catalytic effects of noble metal NPs inevitably decline and may even disappear in some cases. Therefore, specific noble metal NP-ZnO hybrid nanostructures should be designed to possess the advantages of both chemical and electronic sensitization while preserving the stability of noble metal NPs under severe working conditions.

In this paper, we introduce the preparation of novel Au-decorated ZnO nanospheres (Au-ZnO NSs) containing many small Au NPs encapsulated within ZnO NSs and relatively larger Au NPs decorated on the surface of ZnO NSs using laser irradiation of liquids. The Au-ZnO NS-based sensors, as sensing materials, possess combined chemical and electronic sensitization. These sensors exhibited higher sensitivity and lower working temperature toward ethanol molecules compared with pure ZnO NS-based sensors.

Experimental Section

Chemicals and Materials

Sodium hydroxide (NaOH) was purchased from Sinopharm Chemical Reagent Co. Ltd., while Au (99.99%) and Zn (99.99%) metal plates were obtained from Beijing Goodwill Metal Technology Co. Ltd. (Beijing, China). Ultrapure water was prepared using a Milli-Q-Plus system.

Preparation of Au-ZnO NSs

First, Au colloidal solution was obtained by ablating a piece of Au plate for 3 min in an aqueous solution of 1 mM NaOH using a focused laser of 1064 nm wavelength with an energy density of 80 mJ/pulse (Fig. 1 [Figure 1: see original paper]). Then, the precursor colloidal solution containing Au and ZnO NPs was synthesized by immersing the Zn plate in 18 mL of the as-prepared Au colloidal solution. The plate was ablated for 10 min using a focused laser of 1064 nm wavelength with an energy density of 100 mJ/pulse. Subsequently, the mixed

Au and ZnO colloidal solution was further irradiated by an unfocused laser with 355 nm wavelength and energy density of 40 mJ/pulse under continuous stirring for 40 min. The color of the colloidal solution changed from brown to deep purple after irradiation.

Pure ZnO NSs were prepared by similar processes. Zn colloidal solution was prepared by ablating a Zn plate for 10 min in an aqueous solution of 1 mM NaOH using a focused laser of 1064 nm wavelength. Then, the as-prepared Zn colloidal solution was irradiated with an unfocused laser of 355 nm wavelength under the same conditions. The samples were washed several times with deionized water by centrifugation. The products were then collected and annealed in a muffle furnace at 400 °C for 2 h for characterization and gas sensing measurements.

Fig. 1 Scheme of the synthesis of Au-ZnO nanospheres (NSs)

Characterization

The morphology and structure of the products were investigated using field-emission scanning electron microscopy (SU8020) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan). The X-ray diffraction (XRD) patterns of all samples were recorded using a Rigaku X-ray diffractometer (G2234) with Cu-K radiation (= 0.15419 nm). Photoluminescence (PL) measurements were performed with a fluorescence spectrophotometer (F-4600, Hitachi). A Keithley 6487 Source/Measure Unit (SMU) was used to record changes in current and provide a power source during sensor performance testing.

Gas Sensing Test

Gas sensors were fabricated by dispersing the Au-ZnO NSs (or pure ZnO NSs) powders in ethanol and directly coating the powders on the surface of ceramic tubes. Gas sensing measurements were conducted by injecting a certain volume of target gas (e.g., ethanol) into the chamber using a microsyringe. After completion of the gas sensing measurements, target gases in the chamber were released by flowing fresh dried air into the chamber. A constant voltage (3 V) was applied to the sensor, and the current was measured and acquired via SMU. The response of the sensor was calculated as follows:

Response = I_g / I_a

where I_a and I_g are the electric currents of the sensor in air and target gas, respectively.

Results and Discussion

Fig. 2 [**Figure 2: see original paper**] shows scanning electron micrographs of pure ZnO NSs (a) and Au-ZnO NSs (b), transmission electron micrographs (c) and (d), and the corresponding high-resolution transmission electron micrograph (e) of the area marked with a white dotted square in (d). Typical scanning electron micrographs (Fig. 2a) and the size distribution histogram (inset of Fig. 2a) show pure ZnO with spherical morphology and an average size of 69 nm. Decoration with Au NPs resulted in spherical Au-ZnO NSs (Fig. 2b) with an average size of 73 nm (inset of Fig. 2b), which is close to that of pure ZnO NSs. Transmission electron micrographs in Figs. 2c and 2d clearly indicated that Au-ZnO NSs were decorated with a few large Au NPs at the edges of the surfaces and encapsulated with many small Au NPs. The high-resolution micrograph (Fig. 2e) of the area marked with a white dotted square in Fig. 2d reveals the highly crystalline nature of the ZnO NSs. Clear lattice fringes with interplanar spacings of 0.26 and 0.24 nm correspond to the (002) crystalline plane of hexagonal wurtzite ZnO and the (111) crystalline plane of face-centered cubic Au, respectively. The related selected-area electron diffraction pattern (Fig. S1) also indicated the single-crystalline characteristic of ZnO NSs. Furthermore, compared with the products without annealing treatment (Fig. S2), the Au-ZnO NSs remained spherical, and no coagulation of the small Au NPs was found, suggesting that the Au-ZnO NSs were very stable at high temperature.

Fig. 3 [**Figure 3: see original paper**] shows (a) X-ray diffraction patterns of as-prepared Zn colloids, pure ZnO NSs, and Au-ZnO NSs, and (b) photoluminescence spectra of pure ZnO NSs and Au-ZnO NSs excited at 300 nm. The phase structures of as-prepared Zn colloidal NPs, pure ZnO NSs, and Au-ZnO NSs were further identified by XRD characterization. The diffraction patterns in Fig. 3a indicate that all three samples contained ZnO in hexagonal structure (JCPDS card No. 01-076-0704). In contrast, the XRD pattern of Zn colloids shows broadened peaks of ZnO, indicating small ZnO NP size, and three extra peaks with weak diffraction intensity belonging to metallic Zn. Additionally, peaks at 38.2°, 44.4°, and 64.6° in the diffraction pattern of Au-ZnO NSs were indexed to the (111), (200), and (220) planes of cubic metallic Au (JCPDS card No. 00-004-0784), respectively. The room temperature PL spectrum (Fig. 3b) of pure ZnO NSs displays a PL emission peak at 380 nm (3.26 eV), which can be ascribed to the band edge emission of ZnO semiconductor. However, the emission intensity declined dramatically when Au NPs were decorated onto ZnO. This significant decrease in PL emission intensity of Au-ZnO NSs should be attributed to efficient transfer of photogenerated electrons from ZnO to Au, suggesting that significant electronic interactions occurred between Au and ZnO.

The products obtained at different irradiation times (0, 5, 20, and 40 min) were analyzed by TEM to investigate the growth mechanism involved in the synthesis of Au-ZnO NSs (**Fig. 4** [**Figure 4: see original paper**]). The product was composed of short ZnO nanorods with average diameter of 11 nm and length of 30 nm prior to laser irradiation (Fig. 4a). The high-resolution transmission electron micrograph in Fig. 4e displays clear lattice fringes with interplanar spacings of 0.25 and 0.24 nm, corresponding to the (101) plane of hexagonal wurtzite ZnO and the (111) plane of cubic Au, respectively. A few irregular spherical NPs with average size of 40 nm were observed after irradiation for 5 min (Fig. 4b). High-resolution transmission micrographs in Figs. 4f and S3 reveal the polycrystalline structure of these irregular spherical aggregates, which comprised many small rod-like ZnO and a few Au NPs, as indicated by white arrows. Increasing the irradiation time to 20 min resulted in transformation of the irregular aggregates to NSs with average size of 65 nm (Fig. 4c), which already exhibited Au-ZnO hybrid nanostructures (Fig. 4g). Further increase in irradiation time to 40 min resulted in complete consumption of rod-like ZnO nanocrystallines (Fig. 4d) and formation of ZnO NSs (Fig. 4h). However, no obvious increase in ZnO NS size was found compared with the product obtained at 20 min, suggesting that ZnO NS size reached a maximum value under the certain input laser fluence of 40 mJ/pulse. This finding can be reasonably explained by Equation (1), which quantitatively defines the maximum particle size at a given fluence:

$$J = \frac{\pi d_p^3 \rho_p}{6\sigma_\lambda^{abs}} \left[C_p^s (T_m - T_0) + \Delta H_m + C_p^l (T_b - T_m) + \Delta H_b \right]$$

where J is the laser fluence, _ ^abs is the absorption cross-section, d_p is particle diameter, _p is density, C_p^s and C_p^l are heat capacities for solids and liquids, ΔH_m is melting heat, and ΔH_b is boiling heat. Thus, the required laser fluence J* that will heat a particle with diameter d_p from room temperature (T_0) to melting temperature (T_m) and to boiling temperature (T_b) can be determined. The physical and thermodynamic constants were adopted from Perry.

The response properties of MOS are highly dependent on operating temperature. The response of pure ZnO NSs under increasing operating temperature reached a maximum value of 75 at 360 °C, but the optimum operating temperature of Au-ZnO NSs was 320 °C, which was lower than that of pure ZnO NSs (**Fig. 5a** [**Figure 5: see original paper**]). The corresponding response value was 3.4 times higher than that of pure ZnO NSs. Figure 5b shows the real-time responses of Au-ZnO NS-based and pure ZnO NS-based sensors toward different ethanol concentrations (10–200 ppm) at 320 °C and 360 °C, respectively. The response values of both sensors were almost the same at low ethanol concentration (20 ppm). However, the response of the Au-ZnO NS-based sensor increased rapidly and exhibited 2–4 times higher values than that of the pure ZnO NS-based sensor when ethanol concentration exceeded 20 ppm. Plots of response value versus ethanol concentration (Fig. 5c) for both sensors revealed that the responses presented approximate linear correlation with ethanol concentration. Stability is also an important parameter for gas sensors. Figure 5d shows that the response of the Au-ZnO NS-based sensor did not decline and remained constant after six cycled measurements, indicating excellent stability.

The physical heating-melting-evaporation mechanism was considered responsible for Au-ZnO NS formation, similar to the report of Wang et al. ZnO NPs dispersed in liquids were melted under appropriate input laser fluence. Neighboring melted NPs fused together and then remelted into larger NPs due to

Brownian motion. A rapid cooling process caused by surrounding liquids occurred after pulsed laser heating (within 7 ns), leading to ZnO NS formation. Some Au NPs were also melted and encapsulated inside ZnO NSs during the melting and remelting processes, while others were decorated on the ZnO NS surfaces.

Fig. 5 (a) Responses versus operating temperature of pure ZnO NS-based and Au-ZnO NS-based sensors to 100 ppm ethanol. Dynamic ethanol response–recovery transients (b) and responses versus ethanol concentrations plot (c) of pure ZnO NS-based and Au-ZnO NS-based sensors at 360 °C and 320 °C, respectively. (d) Cyclic dynamic response–recovery transient of Au-ZnO NSs to 50 ppm ethanol at 320 °C.

The synergetic effects of Au NPs on the gas sensing performance of ZnO were explored through gas sensor experiments using pure ZnO NSs and Au-ZnO NSs. Selectivity of gas sensor materials is highly significant for practical applications. The selectivity of pure ZnO NS-based and Au-ZnO NS-based sensors toward ethanol was evaluated by testing against various toxic gases: methanol, formaldehyde, acetone, diethyl ether, benzene, toluene, and chlorobenzene. The responses of both sensors toward 100 ppm of different gases at 360 °C and 320 °C are shown in **Fig. 6** [**Figure 6: see original paper**]. The Au-ZnO NS-based sensor exhibited enhanced responses compared with the pure ZnO NS-based sensor for all gases. Both sensors showed good selectivity to ethanol. The Au-ZnO NS-based sensor showed diverse responses to different gases: methanol (19.5), formaldehyde (4), acetone (52.5), diethyl ether (5.3), benzene (10.4), toluene (19.6), and chlorobenzene (10.9). Remarkably, the highest response value of 252 was obtained for ethanol, indicating that Au-ZnO NSs have good selectivity to ethanol.

Different morphologies with various exposed crystal planes are believed to influence gas sensing and photocatalytic behavior of metal oxides due to diverse chemisorption abilities of different exposed faces. The morphology of ZnO could affect the selectivity of pure ZnO-based sensors. Hamedani et al. investigated responses of ZnO with three different morphologies (NP, nanorod, and flower-like) to CO, ethanol, and methane, finding that the NP sensor had good selectivity to ethanol. Therefore, improved ethanol selectivity of the Au-ZnO NS-based sensor could be attributed to the spherical morphology of ZnO and the decorated Au NPs.

We propose a possible gas sensing mechanism for our Au-ZnO NS-based sensor by considering both electronic sensitization and chemical catalytic effects (**Fig. 7** [**Figure 7: see original paper**]). For pure ZnO, oxygen in air can adsorb on its surface and form oxygen anions by capturing electrons from its conduction band, leading to high air resistance of the ZnO sensor due to formation of a depletion layer on the ZnO surface. However, Au NPs in Au-ZnO NSs change the energy band structure of ZnO through formation of Schottky barriers. The work function of Au metal (5.1 eV) is larger than that of ZnO (4.65 eV), so conduction band electrons of ZnO transfer into Au NPs to form depletion layers between the

ZnO shell and Au NPs. In our Au-ZnO NSs, Au NPs were both decorated on the ZnO surface and encapsulated inside. Surface-decorated Au NPs could increase the width of the depletion layer in ZnO caused by oxygen absorption, while numerous smaller encapsulated Au NPs would create numerous depletion layers around them within ZnO. As illustrated in Fig. 7a, these depletion layers might connect with each other and evidently increase the air resistance of the Au-ZnO NS-based sensor. This result agrees well with experimental results showing that the air resistance of the Au-ZnO NS-based sensor (2.1 MΩ) was larger than that of the pure ZnO NS-based sensor (1.7 MΩ), implying that Au-ZnO NSs could display better sensitivity than pure ZnO NSs.

In addition to electronic sensitization, Au NPs serve as excellent catalysts for dissociating molecular oxygen due to their spillover effect. Therefore, more molecular oxygen can be absorbed on the ZnO surface after Au NP decoration. The chemisorbed oxygen anions can react with ethanol molecules to release electrons back to the ZnO conduction band when exposed to reducing gases such as ethanol (Fig. 7b). This process leads to decreased resistance of the ZnO sensor. The higher the amount of chemisorbed oxygen anions, the larger the decrease in resistance. Thus, compared with pure ZnO NS-based sensors, the improved sensitivity of Au-ZnO NS-based sensors toward ethanol can be attributed to both electronic and chemical sensitization.

Fig. 7 Scheme of gas sensing mechanism of Au-ZnO NS-based sensor. (a) Exposure of Au-ZnO NS-based sensor to air results in chemisorption of oxygen molecules onto the ZnO surface through electron trapping. These processes can be catalyzed by Au NPs, forming an electronic depletion layer (represented by light blue region) at the ZnO–air interface. In addition to surface depletion layers, depletion layers also form inside ZnO due to Schottky junction formation between Au and ZnO. The depletion layers both on the surface and inside may connect with each other and make the low-resistance cores discrete, resulting in high sensor resistance in air and small current flow. (b) The width of the surface depletion layer decreases after ethanol gas injection, which reacts with absorbed oxygen species. Then, the surface depletion layers disconnect from the inside ones, and the discrete low-resistance cores become continuous. Consequently, the resistance of the Au-ZnO NS-based sensor decreases dramatically, leading to large current flow.

Conclusion

We demonstrated the preparation of novel Au-ZnO NSs containing many small Au NPs encapsulated within ZnO NSs and relatively larger Au NPs decorated on the ZnO NS surface using a laser irradiation of liquid approach. The Au-ZnO NSs showed perfect structural stability against annealing at 400 °C for 2 h. The heating–melting–evaporation mechanism was responsible for the disappearance of ZnO nanorods and formation of Au-ZnO NSs. The Au-ZnO NS-based sensor benefited from this structural stability as a gas sensing material, displaying good reproducibility with unchanged response value during six cycled measurements. Additionally, the Au-ZnO NS-based sensor showed excellent sensing performance toward ethanol, including improved sensitivity and selectivity and reduced working temperature after Au NP decoration onto ZnO NSs. This improved sensing performance can be attributed to the catalytic effects of surface-decorated Au NPs and the formation of depletion layers induced by encapsulated Au NPs. Thus, such stable hybrid nanostructured Au-ZnO NSs could be promising candidates for gas sensing materials.

References

1. P. Rai, S. M. Majhi, Y. T. Yu and J. H. Lee, RSC Adv., 2015, 5, 76229-76248.
2. T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, Anal. Chem., 1962, 34, 1502-1503.
3. (Note: Reference 3 appears to be missing from the original text)
4. Z. Q. Zheng, J. D. Yao, B. Wang and G. W. Yang, Scientific reports, 2015, 5.
5. Y. Y. Zhao, X. Lai, P. Deng, Y. X. Nie, Y. Zhang, L. L. Xing and X. Y. Xue, Nanotechnology, 2014, 25, 115502.
6. S. R. Ryu, S. G. Ram, H. D. Cho, D. J. Lee, T. W. Kang and Y. Woo, Nanoscale, 2015, 7, 11115-11122.
7. M. Chen, Z. H. Wang, D. M. Han, F. B. Gu and G. S. Guo, J. Phys. Chem. C, 2011, 115, 12763-12773.
8. F. L. Meng, N. N. Hou, Z. Jin, B. Sun, Z. Guo, L. T. Kong, X. H. Xiao, H. Wu, M. Q. Li and J. H. Liu, Sens. Actuators B, 2015, 209, 975-982.
9. H. J. Zhang, R. F. Wu, Z. W. Chen, G. Liu, Z. N. Zhang and Z. Jiao, CrystEngComm, 2012, 14, 1775-1782.
10. F. L. Meng, N. N. Hou, Z. Jin, B. Sun, W. Q. Li, X. H. Xiao, C. Wang, M. Q. Li and J. H. Liu, Sens. Actuators B, 2015, 219, 209-217.
11. W. W. Xia, C. Mei, X. H. Zeng, G. K. Fan, J. F. Lu, X. D. Meng and X. S. Shen, ACS Appl. Mater. Interfaces, 2015, 7.
12. Q. Xiang, G. F. Meng, Y. Zhang, J. Q. Xu, P. C. Xu, Q. Y. Pan and W. J. Yu, Sens. Actuators B, 2010, 143, 635-640.
13. N. Tamaekong, C. Liewhiran, A. Wisitsoraat and S. Phanichphant, Sens. Actuators B, 2011, 152, 155-161.
14. N. P. Herring, K. AbouZeid, M. B. Mohamed, J. Pinsk and M. S. El-Shall, Langmuir, 2011, 27, 15146-15154.
15. X. H. Liu, J. Zhang, L. W. Wang, T. L. Yang, X. Z. Guo, S. H. Wu and S. R. Wang, J. Mater. Chem., 2011, 21, 349-356.
16. J. Zhang, X. H. Liu, S. H. Wu, B. Q. Cao and S. H. Zheng, Sens. Actuators B, 2012, 169, 61-66.
17. J. Guo, J. Zhang, M. Zhu, D. X. Ju, H. Y. Xu and B. Q. Cao, Sens. Actuators B, 2014, 199, 339-345.
18. L. L. Wang, Z. Lou, T. Fei and T. Zhang, J. Mater. Chem., 2012, 22, 4767-4771.
19. X. W. Li, X. Zhou, H. Guo, C. Wang, J. Y. Liu, P. Sun, F. M. Liu and G.

Y. Lu, ACS Appl. Mater. Interfaces, 2014, 6.
20. (Note: Reference 20 appears to be missing from the original text)
21. S. M. Majhi, P. Rai and Y. T. Yu, ACS Appl. Mater. Interfaces, 2015, 7, 9462-9468.
22. P. M. Arnal, M. Comotti and F. Schüth, Angew. Chem. Int. Ed., 2006, 45, 8224-8227.
23. (Note: Reference 23 appears to be missing from the original text)
24. Y. K. Lin, Y.J. Chiang and Y. J. Hsu, Sens. Actuators B, 2014, 204, 190-196.
25. A. Pyatenko, M. Yamaguchi and M. Suzuki, J. Phys. Chem. C, 2007, 111, 7910-7917.
26. H. Q. Wang, A. Pyatenko, K. Kawaguchi, X. Y. Li, Z. Swiatkowska-Warkocka and N. Koshizaki, Angew. Chem. Int. Ed., 2010, 49, 6361-6364.
27. D. W. Green, R. H. Perry, Perry' s Chemical Engineers' Handbook, McGraw-Hill, New York, 1999.
28. X. G. Han, H. Z. He, Q. Kuang, X. Zhou, X. H. Zhang, T. Xu, Z. X. Xia and L. S. Zheng, J. Phys. Chem. C, 2009, 113.
29. N. F. Hamedani, A. R. Mahjoub, A. A. Khodadadi and Y. Mortazavi, Sens. Actuators B, 2011, 156, 737–742.
30. R. K. Joshi, Q. Hu, F. Alvi, N. Joshi and A. Kumar, J. Phys. Chem. C, 2009, 113, 16199-16202.
31. V. Postica, I. Holken, V. Schneider, V. Kaidas, O. Polonskyi, V. Cretu, I. Tiginyanu, F. Faupel, R. Adelung and O. Lupan, Mater. Sci. Semicond. Process., 2016, 49, 20-33.
32. M. Hübner, D. Koziej, J. D. Grunwaldt, U. Weimar and N. Barsan, Phys. Chem. Chem. Phys., 2012, 14, 13249-13254.
33. Q. Xiang, G. F. Meng, H. B. Zhao, Y. Zhang, H. Li, W. J. Ma and J. Q. Xu, J. Phys. Chem. C, 2010, 114, 2049-2055.
34. L. L. Wang, H. M. Dou, Z. Lou and T. Zhang, Nanoscale, 2013, 5, 2686-2691.

Acknowledgement

We thank the financial support from the National Basic Research Program of China (2014CB931704), the National Natural Science Foundation of China (NSFC, No. 11304315, 11204308, 51401206, 11404338, 51371166), and the CAS/SAFEA International Partnership Program for Creative Research Teams.

Electronic Supplementary Information (ESI) available: [additional TEM analysis of Au-ZnO nanospheres]. See DOI: 10.1039/x0xx00000x

Note: Figure translations are in progress. See original paper for figures.