

Monodisperse ZnFe₂O₄ nanospheres synthesized by a nonaqueous route for a highly selective low-ppm-level toluene gas sensor

Dong, Chengjun; Liu, Xu; Xiao, Xuechun; Du, Shangfeng; Wang, Yude

DOI:

[10.1016/j.snb.2016.09.122](https://doi.org/10.1016/j.snb.2016.09.122)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Dong, C, Liu, X, Xiao, X, Du, S & Wang, Y 2017, 'Monodisperse ZnFe₂O₄ nanospheres synthesized by a nonaqueous route for a highly selective low-ppm-level toluene gas sensor', *Sensors and Actuators B: Chemical*, vol. 239, pp. 1231-1236. <https://doi.org/10.1016/j.snb.2016.09.122>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Checked 14.11.16

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Title: Monodisperse ZnFe₂O₄ nanospheres synthesized by a nonaqueous route for a highly selective low-ppm-level toluene gas sensor

Author: Chengjun Dong Xu Liu Xuechun Xiao Shangfeng Du
Yude Wang



PII: S0925-4005(16)31547-7
DOI: <http://dx.doi.org/doi:10.1016/j.snb.2016.09.122>
Reference: SNB 20988

To appear in: *Sensors and Actuators B*

Received date: 10-6-2016
Revised date: 14-9-2016
Accepted date: 21-9-2016

Please cite this article as: Chengjun Dong, Xu Liu, Xuechun Xiao, Shangfeng Du, Yude Wang, Monodisperse ZnFe₂O₄ nanospheres synthesized by a nonaqueous route for a highly selective low-ppm-level toluene gas sensor, *Sensors and Actuators B: Chemical* <http://dx.doi.org/10.1016/j.snb.2016.09.122>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Monodisperse ZnFe₂O₄ nanospheres synthesized by a nonaqueous route
for a highly selective low-ppm-level toluene gas sensor**

Chengjun Dong,^a Xu Liu,^a Xuechun Xiao,^a Shangfeng Du,^b Yude Wang^{c,*}

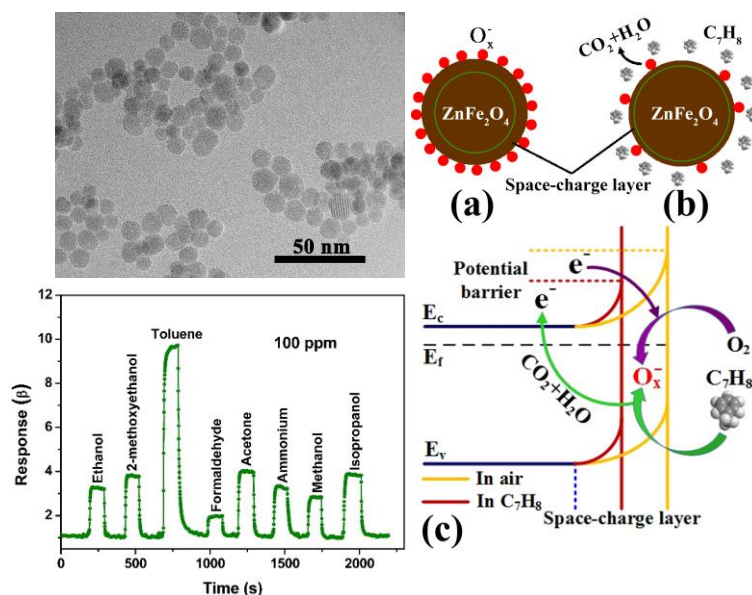
*a School of Materials Science and Engineering, Yunnan University, 650091 Kunming,
People's Republic of China.*

*b School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15
2TT, UK.*

c Department of Physics, Yunnan University, 650091 Kunming, People's Republic of China.

* To whom correspondence should be addressed. Tel:+86-871-65035570; Fax: +86-871-65035376. E-mail:
ydwang@ynu.edu.cn (Y. D. Wang)

Graphical abstract



Highlights

- Monodisperse ZnFe₂O₄ nanospheres were synthesized via a nonaqueous route.
- ZnFe₂O₄ nanospheres have diameters of 7-16 nm and a large surface area of 87.40 m²/g.
- ZnFe₂O₄ nanospheres show a high potential for detecting low-ppm-level toluene.
- ZnFe₂O₄ nanospheres exhibit good linearity with a high response and excellent selectivity.

Abstract

Monodisperse ZnFe₂O₄ nanospheres were successfully synthesized via a nonaqueous route in benzyl alcohol at low temperature of 200 °C. It was found that the ZnFe₂O₄ is 7-16 nm in diameter with a large surface area of 87.40 m²/g. The gas sensor based on ZnFe₂O₄ nanospheres shows a high potential for detecting low-ppm-level toluene, exhibiting a good linearity ranging from 1-100 ppm with a high response (100 ppm: 9.98) and excellent selectivity.

Keywords: ZnFe₂O₄ nanospheres; Nonaqueous synthesis; Gas response; Toluene; Low-ppm-level; Selectivity

1. Introduction

Toluene (C_7H_8) is widely used in chemical industry and found to be neurotoxic, which is harmful to human beings even at a very low concentration [1]. An effective detection of toluene gas is of great benefit to both the environment and our own humanity. Many sensing materials such as SnO_2 [2], ZnO [3], WO_3 [4], $\alpha-Fe_2O_3$ [5], In_2O_3 [6], Co_3O_4 [7], CuO [8], etc., and their hybrids [9,10] have been prepared for toluene detection. However, a highly selective detection of low-ppm-level toluene still remains a great challenge. As a multifunctional n-type semiconductor, $ZnFe_2O_4$ has attracted much attention in the fields of gas sensors, catalysts, magnets, Li-ion batteries and solar cells [11-18]. In particular, the excellent gas-sensing properties of various $ZnFe_2O_4$ materials have been extensively explored in recent years. For instance, the earlier works have been demonstrated, such as $ZnFe_2O_4$ particles to H_2S [14], ultrafine powder to Cl_2 [15], $ZnFe_2O_4/ZnO$ to n-butanol [16], porous $ZnFe_2O_4$ nanospheres to acetone [17], and so on. However, the sensing performances of $ZnFe_2O_4$ towards toluene is yet reported but highly fascinating.

$ZnFe_2O_4$ nanostructures have been prepared through various approaches and investigated for diverse purposes. In which, nonaqueous approaches in organic solvents under exclusion of water have been reported to offer many advantages in controlling synthesis. The organic component in the reaction mixture not only acts as the oxygen supplying agent but also strongly influences products in terms of their particle size, shape, surface and assembly properties [19-21]. Many metal oxide nanoparticles, hybrid nanomaterials, aerogel and thin films with different shapes and sizes have been prepared based on the nonaqueous approach [19-25]. A solvent of benzyl alcohol has typically been used, the group of Niederberger in

particular, to prepare nanocrystals of different metal oxides [19,23,24]. The benzyl alcohol prevents the use of any surfactants and itself may play a multiple role as reaction medium, oxygen supplying and/or capping agent [19].

In this communication, we report the synthesis of monodisperse ZnFe_2O_4 nanospheres by a nonaqueous route and its application for toluene detection. The synthesis was performed at 200 °C for 24 h using nonaqueous zinc acetate and Iron (III) acetylacetonate as precursors and benzyl alcohol as oxygen supplying agent. The obtained ZnFe_2O_4 nanospheres was characterized via X-ray diffraction, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The high sensitivity and excellent selectivity of the ZnFe_2O_4 nanospheres towards toluene detection was evaluated at the operating temperature of 300 °C.

2. Experimental section

2.1 Materials synthesis

All of the analytical grade reagents in this work were purchased from Aladdin and were used directly without any further purification. A typical preparation procedure was as follows: 1 mmol nonaqueous Zinc acetate and 2 mmol Iron (III) acetylacetonate were dissolved in 30 ml benzyl alcohol under stirring for 30 min. Subsequently, the resulting solution was transferred into 50 ml Teflon-lined stainless-steel autoclave. The crystallization was carried out at 200 °C for 24 h. When the autoclave was cooled naturally down to room temperature, the products were washed thoroughly with acetone, ethanol, and deionized water for several times. The final ZnFe_2O_4 powder was collected after dried at 60 °C.

2.2 Materials characterization

The crystal structure and phase identification of the as-synthesized ZnFe_2O_4 were estimated by X-ray diffraction (XRD, Rigaku TTRIII) using $\text{Cu K}\alpha$ 1 radiation (with an incident X-ray wavelength of 1.54056 Å). The energy-dispersive X-ray spectroscopy (EDX) was carried out by a FEI QUANTA 200 equipped with an EDX attachment. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were performed on a JEM-2100 (JEOL, Japan) at an operating acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted using ESCALAB system with $\text{Al K}\alpha$ X-ray radiation under a working voltage of 15 kV. The specific surface area of the as-prepared material was tested using Nitrogen adsorption isotherm method at 77.3 K with a Micromeritics ASAP 2010 automated sorption analyzer. Before the measurement, the sample was degassed under vacuum at 300 °C for 3 h.

2.3 Gas sensor preparation and measurement

The as-synthesized ZnFe_2O_4 nanospheres were used to fabricate gas sensors as following. A certain amount of products were firstly grinded with an appropriate amount of deionized water to form a paste. Then, the paste was carefully painted onto the outside surface of an alumina tube (4 mm in length, 1.2 mm in outside diameter, and 0.8 mm in internal diameter) with a pair of Au electrodes at each end connected by platinum wires. The thickness of sensing materials was about 0.6-0.8 mm.

After being calcined in air at 400 °C for 1 h, a Ni-Cr heating wire was put through the tube and all wires were carefully connected to a Bakelite base to perform electrical measurements using a WS-30 A system. More details were described in the Supplementary Material. For a typical n-type gas sensor, the response (β) was defined as the ratio (R_a/R_g) of

the sensor resistance in dry air (R_a) to that of analytic gas (R_g). The response and recovery times are defined as the time required to reach 90% of the initial equilibrium value.

3. Results and discussion

XRD pattern of the as-synthesized ZnFe_2O_4 sample is shown in Fig. 1. All peaks are well indexed to a cubic ZnFe_2O_4 structure (JPCDS Card No. 74-2397) with space group $Fd\bar{3}m$, indicating no secondary phase formed in the synthesis process. The Rietveld refinement of XRD pattern was conducted using the commonly accepted Maud program developed by Luca Lutterotti [26]. The calculated XRD profile fits well with the experimental data cross the whole tested angles from 10-80°. The structural parameters obtained from the Rietveld refinement are listed in Table S1 in the Supplementary Material. The lattice constant is refined to be 8.4374 Å, which is in close agreement with the standard JCPDS value of 8.4432 Å (JPCDS Card No. 74-2397). Furthermore, the average crystallite size was estimated as 14.5 nm as shown by the broadening XRD peaks. In addition, the EDX results confirm that it is mainly composed Zn, Fe, and O (Fig. S2) with ratio of about 1:2:4, matching the chemical formula of ZnFe_2O_4 .

TEM and HRTEM images are displayed in Fig. 2 to show the fine microstructure of ZnFe_2O_4 product. As expected, the TEM images (Fig. 2 (a) and (b)) show that the ZnFe_2O_4 appears spherical-like morphology with either isolated or as bundles. The diameter of the nanospheres is approximately 7 to 16 nm. HRTEM image of an individual nanosphere (Fig. 2(c)) exhibits sets of lattice fringes with an interplanar distance of 0.478 nm, which is in line with that of (111) facet of ZnFe_2O_4 . From the selected-area electron diffraction (SAED) pattern shown in Fig. 2 (d), diffraction rings are identified as the reflections (111), (220),

(311), (222), (511), and (440) of cubic ZnFe_2O_4 . These findings give additional evidence that the obtained ZnFe_2O_4 nanospheres are highly crystallized, further supporting the above XRD results.

The specific surface area of the ZnFe_2O_4 nanospheres is examined by the nitrogen adsorption-desorption isotherms measurement and a value of $87.40 \text{ m}^2/\text{g}$ was achieved. This large accessible surface area can provide much more active sites for the gas molecules' reaction and hence excellent gas-sensing performances are expected.

The surface chemical states of ZnFe_2O_4 nanospheres were analyzed by XPS (Fig. S5), and core levels of Zn 2p, Fe 2p and O 1s could be identified. Two peaks of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ located at 1022.05 eV and 1045.10 eV with a better symmetry, implying the formation of Zn^{2+} [27]. The XPS of the Fe 2p region is fitted into four contributions. The first two peaks with the binding energy (BE) values of about 712.30 and 719.54 eV are assigned to Fe $2p_{3/2}$ and its shakeup satellite, while the higher BE peaks around 726.02 eV and 734.03 eV correspond to Fe $2p_{1/2}$ and its shakeup satellite, respectively, indicating the presence of the Fe^{3+} cations [28]. In particular, the state of O 1s is well evolved into two distinguishable peaks with BE values of about 530.69 eV (lattice oxygen: $\text{O}_{\text{lattice}}$) and 532.30 eV (adsorbed oxygen: O_{ads}), respectively. The adsorbed oxygen is widely considered to play a critical role for gas detection.

To understand the gas-sensing properties towards toluene, sensors were constructed from the as-prepared ZnFe_2O_4 nanospheres. As shown in Fig. S3 and Table S2, we made comparison between response, response time and recovery time to 100 ppm toluene at typical temperature. At low temperature such as $260 \text{ }^\circ\text{C}$, the response is 79.12, but the gas

sensor takes much longer time to response (>156 s) and recovery (383 s). At higher temperature of 340 °C, although the fast response (6 s) and recovery (8 s) can be obtained, the response reduces to be 3.8. Therefore, taking the gas-sensing properties such as response, response and recovery time, etc., into the overall consideration, an operating temperature of 300 °C was chosen. Fig. 3 (a) shows the actual resistance of the ZnFe₂O₄ sensor exposed to various concentrations of toluene gas ranging from 1-100 ppm. As can be seen, the sensors demonstrated a reduced resistance upon exposure to toluene, typically observing in n-type semiconductor gas sensors. It can be seen that even a very low concentration of toluene, i.e. 1 ppm, can be effectively detected. The corresponding responses are 1.41, 1.83, 2.20, 3.85, 5.15, 6.75, and 9.98 to 1, 5, 10, 30, 50, 70, and 100 ppm toluene, respectively, as plotted in Fig. 3(b). The relationship between the response and toluene concentration (1-100 ppm) shows a very good linearity, that is $\beta=0.08C+1.29$ (here β is the response and C is the toluene concentration) with a relative correlative coefficient $R^2=0.991$ by lineal fitting of the experimental data. The response time and recovery time of the sensor are calculated to be 18.14 and 29.20 s towards 100 ppm toluene, as shown in Fig. 3(c). In addition, the reproducibility of ZnFe₂O₄ sensor was also studied with 100 ppm toluene gas. In Fig. 3(d), the reproducibility test demonstrates that the sensor nearly maintains its initial value of response without a big fluctuation upon five successive sensing tests. Besides, a long-term stability of the ZnFe₂O₄ based sensor has been tested. As shown in Fig. S 4, the sensor exhibits a good stability towards 50 ppm and 100 ppm toluene in 20 days. The mean response are calculated to be 5.23 and 9.99 with changes of $\pm 17\%$ and $\pm 11\%$ for 50 ppm and 100 ppm toluene, respectively. These findings verify our sensor could possess excellent stability

in long term. Previous reports in open literatures about various sensing materials based toluene sensors with distinct morphologies are compared in Table S3. Obviously, the ZnFe_2O_4 nanospheres based sensor in our work possesses a comparable sensing-performance towards toluene.

The selectivity of sensors is also considered as one of the important parameters in their practical applications in guaranteeing exact recognition of a specific target molecule among various gases. Therefore, the response of the ZnFe_2O_4 based sensor to different gases, including ethanol, 2-methoxyethanol, toluene, formaldehyde, acetone, ammonium, methanol and isopropanol, was tested towards a fixed concentration of 100 ppm at the same operating temperature, as comparably summarized in Fig. 4. Apparently, the ZnFe_2O_4 based sensor exhibits a much higher sensitivity to toluene rather than to other tested gases. Several factors might be attributed to the good selectivity with respect to both toluene molecules and ZnFe_2O_4 . Firstly, it is probable that the methyl group ($-\text{CH}_3$) played an important role in enhancing the sensing behavior because of its adsorbing ability [29]. Secondly, lower enthalpy change of the dehydrogenation for toluene possibly results in higher response [30]. Moreover, the small energy difference in terms of lowest unoccupied molecule orbit (LUMO) energy and highest occupied molecule orbit (HUMO) energy between toluene and ZnFe_2O_4 could favor the interaction to take place, which is contributed to the good selectivity of toluene [31].

The gas-sensing mechanism of ZnFe_2O_4 nanospheres can be detailed by following the classical electron depletion theory [32,33] and visibly displayed in Fig. 5. In air, oxygen molecules adsorb on the surface of the sensing materials, and thus capture electrons from the

conduction band of ZnFe_2O_4 to create oxygen species O_{ads} (such as O^- , O^{2-} , and O_2), as shown in XPS analysis (Fig. S5). As a result, the charge concentrations decrease, leading to a widening thickness of the charge accumulation layer (the increase of R_a) (Fig. 5 (a)). After exposing to reducing gas like toluene, toluene molecules react with the adsorbed oxygen species, which is $\text{C}_7\text{H}_8 + \text{O}_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$, releasing the trapped electrons back into ZnFe_2O_4 . Thus the charge concentrations will increase and the thickness of the charge accumulation layer decrease accordingly (the decrease of R_g) (Fig. 5 (b)). Accompanying with the variation of electrons, a contrastive change of the potential barrier as well as space-charge layer are compared in Fig. 5 (c), which is the essence of a semiconductor gas sensor. In brief, the change of resistance is definitely dependent on the sensing material, the chemisorbed oxygen and the tested gas. In our case, the relatively strong interaction between the toluene molecules and the surface oxygen species of ZnFe_2O_4 is the plausible reason for the excellent sensing performance.

Taken together, these results indicate that the ZnFe_2O_4 nanospheres are a promising gas sensing material in detecting low concentration toluene gas in the environment. The good sensing performance is attributed to its native nature, and in particular the high surface area which enables a large exposure of surface atoms to provide more active sites for the absorption of gas molecules and hence facilitate the surface reactions. Very recently, the detection of ppb-level toluene was realized with Pt-functionalized SnO_2 - ZnO core-shell nanowires [9]. Hence, more works are highly desired to further improve the performance of ZnFe_2O_4 nanospheres based sensor by coupling with other sensing materials, doping with approved elements, or functionalizing with noble nanoparticles.

4. Conclusions

In summary, ZnFe₂O₄ nanospheres with 7-16 nm in diameter was prepared by a one-pot solvothermal route using benzyl alcohol as solvent. The native nature and in particular the large specific surface area, 87.40 m²/g, were favorable for the gas sensing performance. Gas-sensing measurements indicated that the ZnFe₂O₄ nanospheres based sensor exhibits a high response and excellent selectivity to the detection of low-ppm-level toluene gas, with a response of 1.41 and 9.98 at 1 and 100 ppm, respectively. A good linearity was achieved within the range of 1-100 ppm. The excellent detection performance, in addition with the simple preparation approach, makes the as-synthesized ZnFe₂O₄ nanospheres a promising material for toluene gas detection at a low concentration.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51262029) and the Project of the Department of Education of Yunnan Province (2015Y008).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:.

References

- [1] World Health Organization, Air quality guidelines for Europe, 2000.
- [2] J. R. Huang, X. J. Xu, C. P. Gu, W. Z. Wang, B. Y. Geng, Y. F. Sun, J. H. Liu, Effective VOCs gas sensor based on porous SnO₂ microcubes prepared via spontaneous phase segregation, *Sensors and Actuators B* 173 (2012) 599–606.
- [3] L. W. Wang, S. R. Wang, M. J. Xu, X. J. Hu, H. X. Zhang, Y. S. Wang, W. P. Huang, A Au-functionalized ZnO nanowire gas sensor for detection of benzene and toluene, *Physical Chemistry Chemical Physics* 15 (2013) 17179–17186.
- [4] Z. H. Li, J. C. Li, L. L. Song, H. Q. Gong, Q. Niu, Ionic liquid-assisted synthesis of WO₃ particles with enhanced gas sensing properties, *Journal of Materials Chemistry A* 1 (2013) 15377–15382.
- [5] S. R. Wang, Y. S. Wang, H. X. Zhang, X. L. Gao, J. D. Yang, Y. Wang, Fabrication of porous α -Fe₂O₃ nanoshuttles and their application for toluene sensors, *RSC Advances* 4 (2014) 30840–30849.
- [6] Z. H. Li, Y. L. Y. X. Luan, J. C. Li, A. X. Song, In (OH)₃ particles from an ionic liquid precursor and their conversion to porous In₂O₃ particles for enhanced gas sensing properties, *CrystEngComm* 15 (2013) 1706–1714.
- [7] C. H. Zhao, B. Y. Huang, J. Y. Zhou, E. Q. Xie, Synthesis of porous Co₃O₄ nanonetworks to detect toluene at low concentration, *Physical Chemistry Chemical Physics* 16 (2014) 19327–19332.
- [8] C. Yang, F. Xiao, J. D. Wang, X. T. Su, A highly sensitive colorimetric sensor for

- adrenaline detection based on organic molecules-functionalized gold nanoparticles, *Sensors and Actuators B* 207 (2015) 277–285.
- [9] J. H. Kim, S. S. Kim, Realization of ppb-scale toluene-sensing abilities with Pt-functionalized SnO₂-ZnO core-shell nanowires, *ACS Appl. Mater. Interfaces*, 7 (2015) 17199–17208.
- [10] H. Shan, C. B. Liu, L. Liu, J. B. Zhang, H. Y. Li, Z. Liu, X. B. Zhang, X. Q. Chi, Excellent toluene sensing properties of SnO₂-Fe₂O₃ interconnected nanotubes, *ACS Appl. Mater. Interfaces*, 5 (2013) 6376–6380.
- [11] L. Lin, Q. M. Pan, ZnFe₂O₄@ C/graphene nanocomposites as excellent anode materials for lithium batteries, *Journal of Materials Chemistry A* 3 (2015) 1724–1729.
- [12] J. A. Gomes, G. M. Azevedo, J. Depeyrot, J. Mastnik-Filh, F. L. O. Paula, F. A. Torunhl, R. Perzynski, Structural, chemical, and magnetic investigations of core-shell zinc ferrite nanoparticles, *Journal of Physical Chemistry C* 116 (2012) 24281–24291.
- [13] R. Dom, R. Subasri, N. Y. Hebalkar, A. S. Chary, P. H. Borse, Synthesis of a hydrogen producing nanocrystalline ZnFe₂O₄ visible light photocatalyst using a rapid microwave irradiation method, *RSC Advances* 2 (2012) 12782–12791.
- [14] C. V. Gopal Reddy, S. V. Manorama, V. J. Rao, Preparation and characterization of ferrites as gas sensor materials, *Journal of Materials Science Letters* 19 (2000) 775–778.
- [15] X. S. Niu, W. P. Du, W. M. Du, Preparation and gas sensing properties of ZnM₂O₄ (M= Fe, Co, Cr), *Sensors and Actuators B* 99 (2004) 405–409.
- [16] S. R. Wang, J. X. Zhang, J. D. Yang, X. L. Gao, H. X. Zhang, Y. S. Wang, Z. Y. Zhu,

- Spinel ZnFe₂O₄ nanoparticle-decorated rod-like ZnO nanoheterostructures for enhanced gas sensing performances, *RSC Advances* 5 (2015) 10048–10057.
- [17] X. Zhou, J. Y. Liu, C. Wang, P. Sun, X. L. Hu, X. W. Li, K. Shimano, N. Yamazoe, C. Y. Lu, Highly sensitive acetone gas sensor based on porous ZnFe₂O₄ nanospheres, *Sensors and Actuators B* 206 (2015) 577–583.
- [18] J. Jeong, J. H. Min, A. Y. Song, J. S. Lee, J. S. Ju, J. H. Wu, Y. K. Kim, Nonaqueous synthesis and magnetic properties of ZnFe₂O₄ nanocrystals with narrow size distributions, *Journal of Applied Physics* 109 (2011) 07B511.
- [19] N. Pinna, M. Niederberger, Surfactant-free nonaqueous synthesis of metal oxide nanostructures, *Angewandte Chemie International Edition* 47 (2008) 5292–5304.
- [20] P. H. Mutin, A. Vioux, Nonhydrolytic processing of oxide-based materials: simple routes to control homogeneity, morphology, and nanostructure, *Chemistry of Materials* 21 (2009) 582–596.
- [21] N. Pinna, The “benzyl alcohol route”: an elegant approach towards organic–inorganic hybrid nanomaterials, *Journal of Materials Chemistry* 17 (2007) 2769–2774.
- [22] F. Rechberger, G. Ilari, M. Niederberger, Assembly of antimony doped tin oxide nanocrystals into conducting macroscopic aerogel monoliths, *Chemical Communication* 50 (2014) 13138–13141.
- [23] F. J. Heiliqtaq, M. J. I. Airaghi Leccardi, D. Erdem, M. J. Süess, M. Niederberger, Anisotropically structured magnetic aerogel monoliths, *Nanoscale* 6 (2014) 13213–13221.

- [24] L. Luo, D. Bozyigit, V. Wood, M. Niederberger, High-quality transparent electrodes spin-cast from preformed antimony-doped tin oxide nanocrystals for thin film optoelectronics, *Chemistry of Materials* 25 (2013) 4901–4907.
- [25] G. Clavel, E. Rauwel, M. G. Willinger, N. Pinna, Non-aqueous sol–gel routes applied to atomic layer deposition of oxides, *Journal of Materials Chemistry* 19 (2009) 454–462.
- [26] M. Ferrari, L. Lutterotti, Method for the simultaneous determination of anisotropic residual stresses and texture by X - ray diffraction, *Journal of Applied Physics* 76 (1994) 7246–7255.
- [27] X. H. Liu, J. Zhang, X. Z. Guo, S. H. Wu, S. R. Wang, Amino acid-assisted one-pot assembly of Au, Pt nanoparticles onto one-dimensional ZnO microrods, *Nanoscale* 2 (2010) 1178–1184.
- [28] T. Yamashita, P. Hayes, Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials, *Applied Surface Science* 254 (2008) 2441–2449.
- [29] Y. J. Kwon, H. G. Na, S. Y. Kang, S. W. Choi, S. S. Kim, H. W. Kim, Selective detection of low concentration toluene gas using Pt-decorated carbon nanotubes sensors, *Sensors and Actuators B* 227 (2016) 157-168.
- [30] F. Li, C. Li, L. H. Zhu, W. B. Guo, L. Shen, S. P. Wen, S. P. Ruan, Enhanced toluene sensing performance of gold-functionalized WO₃·H₂O nanosheets, *Sensors and Actuators B* 223 (2016) 761-767.
- [31] S. Yang, Y. L. Liu, W. Chen, W. Jin, J. Zhou, H. Zhang, G. S. Zakharova, High sensitivity and good selectivity of ultralong MoO₃ nanobelts for trimethylamine gas,

Sensors and Actuators B 226 (2016) 478-485.

- [32] T. Wanger, S. Haffer, C. Weinberger, D. Klaus, M. Tiemann, Mesoporous materials as gas sensors, *Chemical Society Review* 42 (2013) 4036–4053.
- [33] Y. F. Sun, S. B. Liu, F. L. Meng, J. Y. Liu, Z. Jin, L. T. Kong, J. H. Liu, Metal oxide nanostructures and their gas sensing properties: a review, *Sensors* 12 (2012) 2610–2631.

Biographies

Chengjun Dong received his PhD in Materials Physics and Chemistry from Jilin University, China, in 2013. During pursuing his doctoral degree, he was a visitor in Collins research group at University of California, Irvine from 2011-2013. Since 2013, he has been working at the School of Materials Science and Engineering, Yunnan University, China. His current research activities include the synthesis of functional materials and their applications for chemical and biochemical sensors.

Xu Liu received his B.S. degree in School of Materials Science and Engineering from Yunnan University in 2015. He is currently a graduate student in Yunnan University and devotes to nanostructured metal oxides and their applications in gas sensors and supercapacitor.

Xuechun Xiao is currently a PhD student in Yunnan University and devotes to nanostructured functional materials and their applications in gas sensors and biochemical sensors.

Shangfeng Du received his BEng (1999) degree in Materials Science and Engineering from Tsinghua University and his PhD degree (2005) in Chemical Engineering from the Institute of Process Engineering, Chinese Academy of Sciences, China. He joined the Centre for Hydrogen and Fuel Cell Research (former Fuel Cells Research Group) in the School of Chemical Engineering at the University of Birmingham, as a Marie Curie Research Fellow sponsored by European Commission. His Research interests lies in the interdisciplinary area of materials science and nanotechnology, and in particular on the development of multi-functional nanostructured materials for fuel cell electrodes.

Yude Wang obtained his M.S. degree in Physics Condensed State from Yunnan University in 1997 and Ph.D. in Materials Physics and Chemistry from Tsinghua University in 2003. From 2005 to 2007, he was a guest scientist in Max-Planck-Institute of Metal and an Alexander von Humboldt fellow in Max-Planck-Institute of Colloids and Interfaces, Germany. Currently, he is a professor at the Department of Physics, Yunnan University. His work is devoted to chemical and biochemical sensors, nanostructured functional materials and their applications.

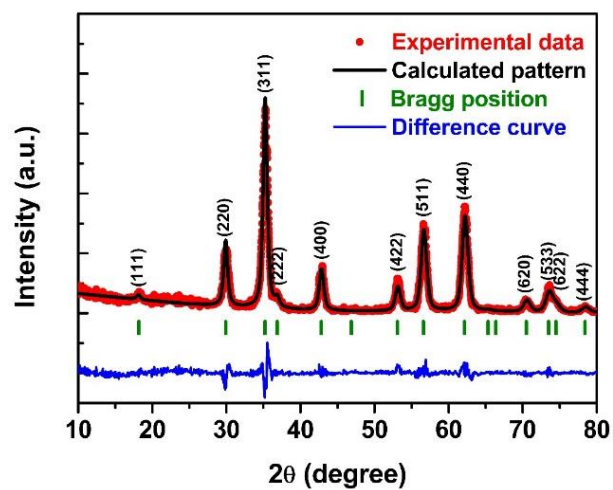


Fig. 1 XRD Rietveld refined patterns (calculated pattern (black) and difference curve (blue)) with the experimental data (Red) of ZnFe₂O₄ nanospheres. The olive short vertical bars stand for the positions of the Bragg reflections.

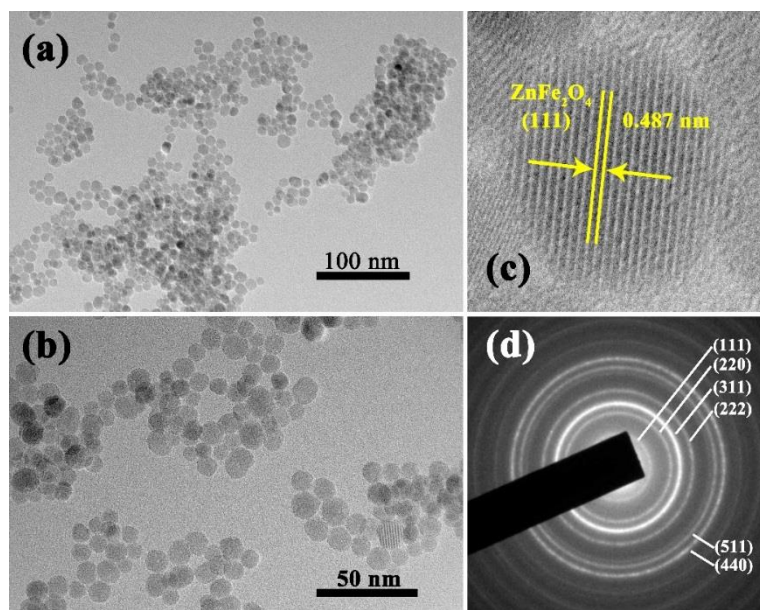


Fig. 2 Low-magnification (a) and high-magnification (b) TEM images of ZnFe₂O₄ nanospheres. The HRTEM image of an individual ZnFe₂O₄ nanosphere (c) and the corresponding SAED pattern (d).

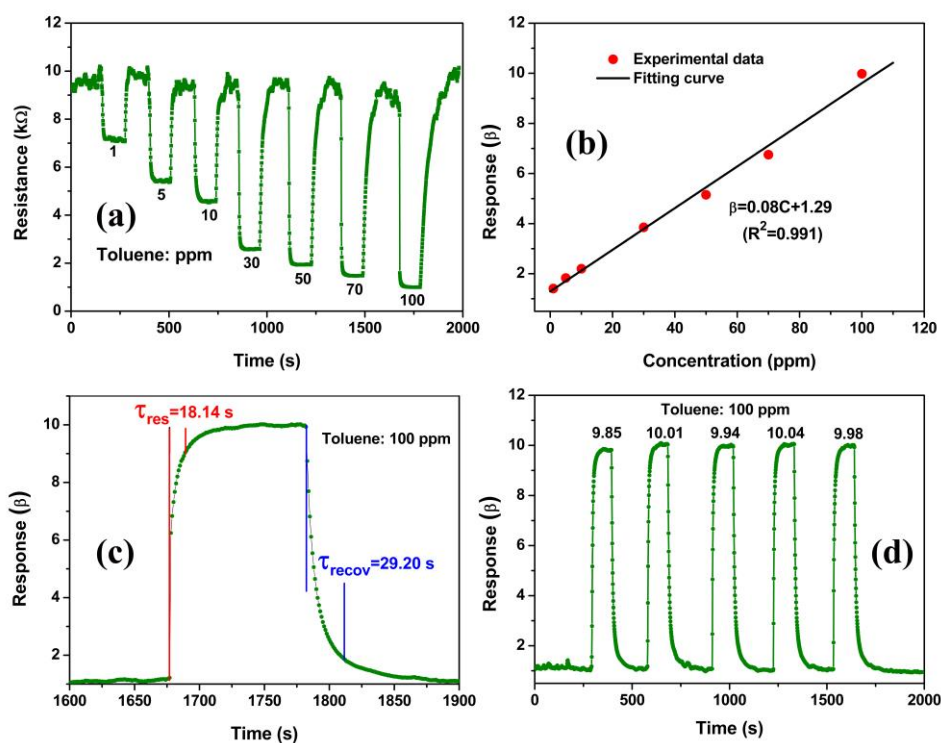


Fig. 3 (a) The dynamic resistance of ZnFe₂O₄ based sensor to toluene gas within the concentration range of 1-100 ppm. (b) The relationship between the gas response and toluene concentration. (c) The typical response and recovery time of ZnFe₂O₄ sensor to 100 ppm toluene gas. (d) Reproducibility of ZnFe₂O₄ sensor on successive exposure to 100 ppm toluene gas with 5 cycles. (All the tests were operated at 300 °C.)

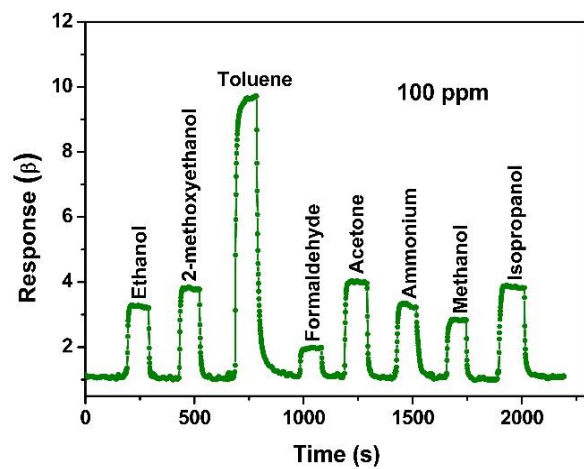


Fig. 4 Selectivity of the ZnFe_2O_4 based sensor to various gases with a concentration of 100 ppm at 300 °C.

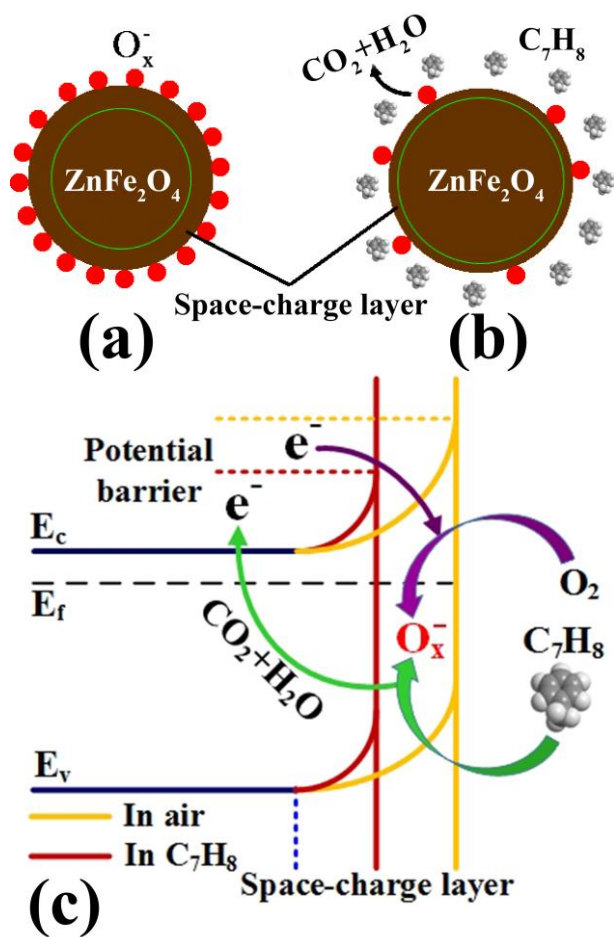


Fig. 5 Schematic diagram of the mechanism for toluene gas sensing in air (a) and toluene (b)

with a contrastive change (c).