# 我们的榜样|徐永善：百舸争流 奋楫者先

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徐永善，男，25岁，一个心怀科研梦想的物理科学学院2017级材料工程硕士研究生。在校期间，他学习成绩优秀，学位课加权平均分93.11分。毕业时，以第一作者发表中科院一区SCI论文8篇，总影响因子超过60，合作发表多篇SCI论文，多次参加国际/国内的学术会议并作墙报展示。曾获2020年"山东省优秀学生"、2019年研究生"国家奖学金"、2019年"青岛大学研究生学术之星"、2019年"青岛大学优秀学生"等荣誉与奖励。

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# Platinum single atoms on tin oxide ultrathin films for extremely sensitive gas detection†

Yongshan Xu,[a] Wei Zheng,[a] Xianghong Liu, *[ab] Liqiang Zhang,[c] Lingli Zheng,[a] Chen Yang,[a] Nicola Pinna[d] and Jun Zhang *[ab]

**Single atom Pt functionalized $SnO_2$ ultrathin films are synthesized by atomic layer deposition (ALD) for application as sensing layers in resistive gas sensors. Here it is shown that the electronic conductivity of the $SnO_2$ ultrathin films is very sensitive to the exposure to triethylamine (TEA), and that the thickness of the $SnO_2$ films (from 4 to 18 nm) has a crucial effect on the sensor response. The 9 nm thick $SnO_2$ film shows the best response to TEA, while a further decrease in the film thickness, *i.e.*, 4 nm, leads to a very weak response due to the two orders of magnitude lower carrier concentration. Single atom Pt catalysts deposited on the 9 nm $SnO_2$ film result in an unexpectedly high enhancement in the sensor response and also a decrease of the sensor working temperature. Consequently, Pt/$SnO_2$ thin film sensors show the highest response of 136.2 to 10 ppm TEA at an optimal temperature of 200 °C (that of a pristine $SnO_2$ film sensor is 260 °C), which is improved by a factor of 9 compared to that of pristine $SnO_2$. Moreover, the Pt/$SnO_2$ sensor exhibits an ultrahigh sensitivity of 8.76 $ppm^{-1}$ and an extremely low limit of detection (LOD) of 7 ppb, which to our best knowledge are far superior to any previous report. Very fast response and recovery times (3/6 s) are also recorded, thus making our sensor platform highly suitable for highly-demanding applications. Mechanistic investigations reveal that the outstanding sensing performances originate from the synergistic combination of the optimized film thickness comparable to the Debye length of $SnO_2$ and the spillover activation of oxygen by single atom Pt catalysts, as well as the oxygen vacancies in the $SnO_2$ films.**

### New Concepts

Herein, we report the conceptual demonstration of single atom Pt functionalized $SnO_2$ ultrathin films by atomic layer deposition (ALD) and their utilization as sensing layers for gas sensors achieving record sensitivity towards detection of VOCs. This work differs from existing research in both fundamental mechanistic research and technological potential in developing sensing materials for advanced sensors. Platinum single atoms are, for the first time, employed to improve the sensing properties of $SnO_2$ film sensors, enabling an exceptionally high sensitivity of 8.76 $ppm^{-1}$ and an extremely low detection limit of 7 ppb, as well as very fast response and recovery, which to our best knowledge are far superior to those previously reported. Our mechanistic investigations reveal that the outstanding sensing performances originate from the spillover activation of oxygen by the single atom Pt catalyst, which has been a critical question in the area of gas sensing materials. Furthermore, the optimized film thickness comparable to the Debye length of $SnO_2$ and the oxygen vacancies in the $SnO_2$ films also play a role in the sensor response. In a broader context, this work presents a breakthrough in the fundamental research of single atom Pt catalysts and $SnO_2$ ultrathin films in application to gas sensors, which has paramount significance in future sensor networks and the Internet of things.

## 1. Introduction

The fast development of the Internet of things (IoT) requires miniaturized and low power consumption gas sensors that are capable of rapidly detecting trace gases, allowing building vast and smart sensor networks.[1] Gas sensors are widely used to monitor gas leakage and air pollution and for household security, as well as in some emerging areas such as exhaled breath diagnosis for the sake of the safety and health of people.[2–6] During the past few decades, nanostructured materials including nanowires, nanosheets and 3D architectures have demonstrated great superiority as sensing layers in chemiresistive sensor devices to achieve high sensitivity to particular target molecules.[7–11] Various nanostructures produced by solution processes such as solvothermal or hydrothermal methods generally appear as powdery materials. These materials are usually made into sensing layers by using methods like screen-printing,

[a] *College of Physics, Center for Marine Observation and Communications, Qingdao University, Qingdao 266071, China. E-mail: xianghong.liu@qdu.edu.cn, jun@qdu.edu.cn*

[b] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China*

[c] *Clean Nano Energy Center, State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China*

[d] *Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany*

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# Highly sensitive and selective detection of acetone based on platinum sensitized porous tungsten oxide nanospheres

Yongshan Xu[a], Chengming Lou[a], Lingli Zheng[a], Wei Zheng[a], Xianghong Liu[a,b], Mahesh Kumar[c], Jun Zhang[a,b,*]

[a] College of Physics, Center for Marine Observation and Communications, Qingdao University, Qingdao 266071, China
[b] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China
[c] Department of Electrical Engineering, Indian Institute of Technology Jodhpur, Jodhpur-342037, India

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ABSTRACT

Metal oxide semiconductors (MOS) are important candidates as the sensing layer for chemical gas sensors to detect volatile organic compounds (VOCs). However, the low surface activity limits the use of MOS in future high performance gas sensors. The design of susceptive nanostructures with prominent surface modification can be an effective strategy to achieve high sensitivity and high selectivity. Herein, Pt nanoparticles with a fine size of below 1 nm serving as the sensitizers are functionalized on porous $W_{18}O_{49}$ nanospheres *via* atomic layer deposition and investigated for acetone detection. The $W_{18}O_{49}$/Pt spheres combine the advantages of fast gas diffusion enabled by the porous shells and catalytic properties of Pt nanocatalysts. Gas sensing tests reveal that $W_{18}O_{49}$/Pt has a very high response to 20 ppm acetone ($R_a/R_g$ = 85), which is ~40 times higher than that of pure $W_{18}O_{49}$ ($R_a/R_g$ = 2.1) at a low operating temperature of 180 °C. Meanwhile, $W_{18}O_{49}$/Pt shows fast response-recovery speed and good stability as well as excellent selectivity to acetone against other interfering gases. In addition, an ultrahigh sensitivity of 1.01 $ppm^{-1}$ and a very low limit of detection of 52 ppb is obtained. The superior gas sensing performances of the $W_{18}O_{49}$/Pt materials indicates a strong potential for detection of biomarkers for exhaled breath diagnosis, and also paves the way to manipulate other metal oxide semiconductor-based sensors with high performances.

## 1. Introduction

The small crystal size and large specific surface area of nanostructured materials afford the great potential as building blocks for application in gas detection [1]. Consequently, nanostructured metal oxides, such as $SnO_2$ [2], ZnO [3,4], $WO_3$ [5–7], $In_2O_3$ [8,9], $Fe_2O_3$ [10] have been extensively manufactured to monitor the environmentally hazardous gases such as $NO_2$ [4], triethylamine [9], $NH_3$ [11], as well as to diagnose disease through exhaled breath analysis. For instance acetone [2,3,5,8,10], has been utilized as a biomarker for diabetes [12]. It is reported that the concentration of acetone in exhaled breath of diabetes is around 1800 ppb, which is higher than that (300 − 900 ppb) of healthy people [13]. Therefore, an accurate detection of acetone of trace concentration is urgently needed.

Although the sensors based on some metal oxide semiconductors (MOSs) have been studied for exhaled breath diagnosis, the MOSs still suffer from high operating temperature, low sensitivity or high limit of detection (LOD). Due to the electronic or chemical promotion effect, noble metal nanoparticles (e.g. Au, Ag, Pt) can serve as sensitizers to significantly enhance the gas sensing properties of MOSs. Choi et al. reported that Pt-functionalized $WO_3$ hemitube exhibited superior acetone response ($R_a/R_g$ = 4.11 at 2 ppm) and low LOD of 120 ppb [13]. Lu et al. reported Rh modification could improve the response of $SnO_2$ to 50 ppm acetone from 6.3–60.6 at 200 °C [14]. Jeong and coworker demonstrated that Pt loaded $SnO_2$ nanofibers exhibited a response of 141.9 to 5 ppm acetone and ultralow LOD of 5 ppb at a temperature of 350 °C [2]. To fabricate the noble metal loaded MOSs, the common synthetic approach mainly includes stirring reduction method [9], polyol reduction method [2], polymer network gel method [4], co-electrospinning method [8], and polymeric fiber templating route [13]. We previously reported an in-situ redox method to produce various types of sensors based on noble metal/MOSs hybrids [15–20]. However, it is difficult to achieve uniform loading of metal nanoparticles on micro- and nanostructured materials with high surface area. Alternatively, atomic layer deposition (ALD), based on self-limiting reactions [21], has demonstrated great advantages in growing

* Corresponding author at: College of Physics, Center for Marine Observation and Communications, Qingdao University, Qingdao 266071, China.
*E-mail address:* jun@qdu.edu.cn (J. Zhang).

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# Multi-metal functionalized tungsten oxide nanowires enabling ultra-sensitive detection of triethylamine

Yongshan Xu[a], Tiantian Ma[a], Yingqiang Zhao[b], Lingli Zheng[a], Xianghong Liu[a,c,*], Jun Zhang[a,c,*]

[a] College of Physics, Qingdao University, Qingdao 266071, China
[b] College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China
[c] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

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ABSTRACT

Sensitization of metal oxide semiconductors is crucial for developing high performance electronic gas sensors. Herein, a unique dual sensitization protocol is proposed to boost the sensing performances of metal oxide nanowires. As a proof-of-concept, $W_{18}O_{49}$ nanowires are selected as the host materials, and Ag, Pt nanoparticles are loaded on $W_{18}O_{49}$ by an *in-situ* redox reaction to fabricate the novel Ag/Pt/$W_{18}O_{49}$ hybrid nanowires. Gas sensing tests demonstrate the superiority of the ternary nanowires in detecting triethylamine vapor against the binary Ag/$W_{18}O_{49}$ and Pt/$W_{18}O_{49}$ nanowires. The sensor based on Ag/Pt/$W_{18}O_{49}$ nanowires manifests fast response and recovery features and very high response over a wide concentration of 0.1–50 ppm, as well as good selectivity and stability. An ultrahigh sensitivity of 1.13 $ppm^{-1}$ is registered by the Ag/Pt/$W_{18}O_{49}$ nanowires and a low detection limit of 71 ppb is obtained. The excellent performances are attributed to the dual sensitization mechanism, i.e., a synergy of both electronic and chemical interactions derived from the Ag and Pt functionalization. This work establishes a new strategy for constructing multi-metal functionalized nanowires and their utilization in functional nanodevices with enhanced performances.

## 1. Introduction

Advanced sensor technology is becoming more and more important in various aspects of modern society, e.g., improving air quality, public healthcare conditions and life quality, etc. [1–3]. Over the past decades, chemiresistive gas sensors based on metal oxide semiconductors (MOSs), such as $SnO_2$, $WO_3$, and ZnO, have been extensively studied and used in monitoring gas leakage, alcohol breath detectors, and exhaled diagnosis [4–8], owing to their outstanding properties like high sensitivity, low-cost, easy production and reliability [1,9]. The principle of MOSs gas sensors is based on the resistance/conductance change, which is caused by the variation in surface electron depletion layers (EDLs) in n-type MOSs and hole accumulation layers in p-type MOSs. The depth of EDLs can be modified significantly by the electron transfer taking place in the process of surface oxygen adsorption or redox reactions occurring between target molecules and ionized oxygen species [10,11].

MOSs gas sensors are commonly evaluated by the “4S” parameters, i.e., sensitivity, speed, selectivity and stability [1]. Among the widely used MOSs, tungsten oxide have drawn considerable interests due to its interesting morphology-dependent response to a variety of molecules including acetone, $H_2$, methanol and $NO_2$ [12–14]. However, current gas sensors based on tungsten oxides still suffer from a poor selectivity and low sensitivity to a particular analyte, which severely limits their utilization in a practical device. To improve the sensor performance, noble metals (e.g., Ag, Pt, and Au) have been employed to sensitize the MOSs, utilizing their catalytic or electronic sensitization effect [9,10,15]. For example, Deng et al. have synthesized mesoporous Pt/$WO_3$ composite via a multicomponent co-assembly approach, which exhibited a high sensitivity to CO gas even at low temperature [9]. Kim et al. have synthesized diverse Pt-based bimetallic $WO_3$ nanofibers by using protein template and found that these structures demonstrated unprecedented sensing performance for detecting biomarkers in human breath [10]. For fabrication of metal/MOSs functional materials, the generation and loading of metal nanoparticles on MOSs is the crucial step. Our group previously reported a general method for construction of various metal/MOSs hybrids using lysine as both the capping and linker agents [16,17]. Xi and co-works have demonstrated the synthesis of noble metal/$WO_3$ nanocomposites through an *in-situ* redox reaction between weakly reductive $WO_{2.72}$ and oxidative metal salts [18]. Nevertheless, a facile procedure for manipulating multiple-metal functionalized MOSs functional materials for advanced sensor devices is

* Corresponding authors at: College of Physics, Qingdao University, Qingdao 266071, China.
*E-mail addresses:* xianghong.liu@qdu.edu.cn (X. Liu), jun@qdu.edu.cn (J. Zhang).

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# Rational design of Au/$Co_3O_4$-functionalized $W_{18}O_{49}$ hollow heterostructures with high sensitivity and ultralow limit for triethylamine detection

Yongshan Xu[a], Tiantian Ma[a], Lingli Zheng[a], Li Sun[a], Xianghong Liu[a,b,*], Yingqiang Zhao[c,**], Jun Zhang[a,b,*]

[a] College of Physics, Qingdao University, Qingdao 266071, China
[b] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China
[c] College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China

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ABSTRACT

The rational design of heterostructures is highly important for innovative sensor technology to acquire efficient gas detection with optimized gas sensing properties. In the present work, a novel heterostructure of Au/$Co_3O_4$/$W_{18}O_{49}$ hollow spheres is constructed and applied for gas sensor application. The structure-property correlation has been studied by means of X-ray diffraction, X-ray photoelectron spectroscopy, Scanning electron microscope and Transmission electron microscope, as well as comprehensive gas sensing tests. Experiments demonstrate that the Au/$Co_3O_4$/$W_{18}O_{49}$ heterostructure delivers outstanding performances in terms of high sensitivity, fast response-recovery, good selectivity, and very low limit of detection against pristine $W_{18}O_{49}$ and $Co_3O_4$/$W_{18}O_{49}$. Notably, a very high response (16.7) to 2 ppm triethylamine and a state-of-the-art limit of detection (81 ppb) are obtained. The superior gas sensing properties are attributed to a synergistic combination of the unique porous structure, the p-n heterojunctions between $Co_3O_4$/$W_{18}O_{49}$, and the catalytic spillover effect of Au nanoparticles.

## 1. Introduction

Triethylamine (TEA) is highly flammable and toxic, and is widely used in pharmaceutical and pesticide production. Exposure to TEA can causes great damage to human health such as serious eye irritation and acute skin corrosion and respiratory difficulty [1–3]. The European Commission has recommends an occupational exposure limit of 1 ppm (8 h TWA) for TEA [4]. Traditional methods such as chromatography and colorimetric techniques [5,6] for tracing TEA have drawbacks in real time monitoring in actual site, time-consuming, high cost, and inconvenience. Therefore, it is highly desirable to develop fast and accurate detection technology with high sensitivity and low limit of detection (LOD).

Gas sensors based on metal oxide semiconductors (MOSs) have many favorable advantages such as low cost, high sensitivity, and portability [7–11], and have attracted great interest in monitoring environmental pollution. N-type MOSs including $SnO_2$, ZnO, and $WO_3$ have been extensively studied as gas sensing materials due to their high sensitivity to a variety of gases [12–17]. However the poor selectivity of MOSs towards a particular gas greatly hinders their practical and real application. Great effort has been explored to optimize the sensor selectivity and typical strategies include functionalization of MOSs with noble metals by virtue of either catalytic or electronic sensitization [18–22], fabrication of complex nanostructures such as multi-shell or yolk-shell hollow spheres [23–26], and construction of heterostructures such as n-p heterojunctions [27–30], as well as coating MOSs with a separation layer such as zeolites and metal organic frameworks [31–33]. Although these approaches are effective to improve the sensor selectivity towards ethanol, formaldehyde, and carbon monoxide, etc., the highly sensitive and the selective detection of TEA at ppb level still remains a challenge.

$W_{18}O_{49}$, consisting of $WO_6$ octahedra sharing corners and edges (Fig. 1a), is formed by crystallographic shear (CS) mechanism to minimize the loss of oxygen from stoichiometric $WO_3$. $W_{18}O_{49}$ has received much interests for gas sensing due to the defect structure and oxygen deficiency [34,35]. For example, the modification of $W_{18}O_{49}$, such as $WO_3$/$W_{18}O_{49}$ [36], urchin-like Pd/$W_{18}O_{49}$ [37], $W_{18}O_{49}$/rGO composites [38], $TeO_2$/$W_{18}O_{49}$ [39] and $TiO_2$/$W_{18}O_{49}$ [40] has led to improved sensor properties for detection of $NH_3$, $H_2$, and $NO_2$. In particular, $W_{18}O_{49}$ nanowires [38,40–43] have been extensively studied for detecting $H_2$, $NO_2$, and $NH_3$, while the gas sensing capability of $W_{18}O_{49}$ hollow spheres are rarely reported.

* Corresponding authors at: College of Physics, Qingdao University, Qingdao 266071, China.
** Corresponding author.
*E-mail addresses:* xianghong.liu@qdu.edu.cn (X. Liu), marszhao@sdnu.edu.cn (Y. Zhao), jun@qdu.edu.cn (J. Zhang).

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# Heterostructures of hematite-sensitized $W_{18}O_{49}$ hollow spheres for improved acetone detection with ultralow detection limit

Yongshan Xu[a], Tiantian Ma[a], Lingli Zheng[a], Yingqiang Zhao[b], Xianghong Liu[a,c,*], Jun Zhang[a,c,*]

[a] College of Physics, Qingdao University, Qingdao 266071, China
[b] College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China
[c] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

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ABSTRACT

Heterostructures of metal oxide semiconductors present great potential for chemical sensor devices due to the fascinating properties endowed by the multiple materials and the heterointerface. In the present work, $W_{18}O_{49}$/$\alpha$-$Fe_2O_3$ hollow heterostructures with different $\alpha$-$Fe_2O_3$ contents are prepared by a hydrothermal method. The chemical composition and structure properties are characterized by multiple techniques. The gas sensing study demonstrates that the $W_{18}O_{49}$/$\alpha$-$Fe_2O_3$ hollow heterostructures exhibit superior sensing performances toward acetone against pure $W_{18}O_{49}$. The composite containing 6.3 wt% $\alpha$-$Fe_2O_3$ delivers the best sensor response and fast response–recovery speed (10 and 31 s), good selectivity, and low limit of detection (86 ppb). The superior gas sensing performance is interpreted by the functions of porous hollow structure and heterojunctions when introducing $\alpha$-$Fe_2O_3$. This work provides a novel structure design for synthesis of high performances gas sensing materials for ppb-level acetone detection.

## 1. Introduction

Metal oxide semiconductors (MOSs) gas sensors have attracted numerous attention in the detection of toxic and flammable gases, as well as the breath analysis for their prominent advantages, such as low cost, high sensitivity, portability and real-time monitoring [1–3]. Acetone, as a volatile organic compound, is widely used in industrial application and laboratories [4]. It is worth noting that acetone can cause the damage to the eyes, nose, skin and nervous system at the concentration higher than 173 ppm [4,5]. In addition, acetone can be used as a biomarker of diabetes that presents in the exhaled breath of patients. Therefore, a noninvasive, rapid and selective detection technique for exhaled breath analysis has been very challenging.

Among the various MOSs investigated for acetone sensing, ZnO [6–8], $WO_3$ [9,10], $In_2O_3$ [11–13], $TiO_2$ [14–16], $SnO_2$ [17–19], etc., have been reported. However, these sensor materials suffer from deficient sensing properties like low sensitivity, long response time, poor selectivity and high limit of detection (LOD). To overcome these issues, one of the effective strategies is to decorate MOSs with noble metals or constructing the heterostructures such as n-n and p-n heterojunctions combined with complex nanostructures [2,20,21]. For example, Xing et al. reported $In_2O_3$/Au nanorods sensor, which shows the ability to detect acetone in exhaled breath with a low detection limit of 0.1 ppm [13]. Lu et al. have demonstrated that the response of Rh modified $SnO_2$ nanofibers to 50 ppm acetone was 60.6, which was 9.6 times higher than that of pure $SnO_2$ [18]. Koo and co-workers displayed that PdO functionalized $Co_3O_4$ hollow nanocages could detect 0.1 ppm acetone [22]. Very recently, Lee's group reported the Pt-decorated Al/ZnO nanoparticles have a short response time of 2.9 s to 10 ppm acetone [7]. However, the use of noble metals commonly increases the fabrication cost of the sensor materials, and the highly sensitive and selective detection of acetone at ppb level still remains a challenge.

$W_{18}O_{49}$, as a wide bandgap n-type semiconductor, has been considered to be a promising sensing material due to its oxygen-deficient structure [23]. Various nanostructures including $W_{18}O_{49}$ nanowires [24,25], mesoporous $W_{18}O_{49}$ mesocrystals [23], $W_{18}O_{49}$/$TiO_2$ and $RuO_2$/$W_{18}O_{49}$ heteronanowires [26,27] have been investigated for detection of $NO_2$ gas. Few sensor reports have been demonstrated for $W_{18}O_{49}$ hollow structures [28], and especially the capability of $W_{18}O_{49}$ for detecting acetone has been rarely reported.

In the present work, we develop a highly sensitive and selective acetone sensor realized by growing $\alpha$-$Fe_2O_3$ sensitizers on $W_{18}O_{49}$ hollow spheres with laminar and porous shells. This material combines the advantages of porous structure to facilitate gas diffusion and adsorption, as well as the function of heterostructure to modify the charge transfer at the interface. Gas sensing experiments show that the

* Corresponding authors at: College of Physics, Qingdao University, Qingdao 266071, China.
*E-mail addresses:* xianghong.liu@qdu.edu.cn (X. Liu), jun@qdu.edu.cn (J. Zhang).

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# Highly sensitive and selective electronic sensor based on Co catalyzed $SnO_2$ nanospheres for acetone detection

Yongshan Xu[a], Lingli Zheng[a], Chen Yang[a], Xianghong Liu[a,b,*], Jun Zhang[a,b,*]

[a] College of Physics, Qingdao University, Qingdao 266071, China
[b] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

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ABSTRACT

Efficient electronic sensors for detection of volatile organic compounds are increasingly in great demand due to its indispensable utilization in healthcare and environment monitoring systems. Assembly of complex nanostructures from diverse host and guest materials proves to be an effective way to create new sensing materials with improved performances. Yet it still remains a challenge to manipulate efficient heterostructures for acetone detection to acquire high sensitivity and selectivity. Herein, a high performance nanosensor is realized based on p-type $Co_3O_4$ sensitized n-type $SnO_2$ porous nanospheres. The rich grain boundaries between adjacent $SnO_2$ nanoparticles serve as the active sites for molecules adsorption and electron transportation. The p-n heterointerface formed between $Co_3O_4$ and $SnO_2$ allows for the fast sensing reactions on materials surface. Consequently, the sensor device delivers outstanding properties in terms of fast response-recovery, low detection limit (103 ppb), high sensitivity and excellent selectivity toward acetone detection. The strategy presented here is generally applicable and can provide some hints to design efficient electronic sensors with an optimized selectivity.

## 1. Introduction

Detection of volatile organic compounds (VOCs) is technically important in industrial production and laboratory environment [1,2]. In particular, acetone detection has drawn increasing attention due to its fascinating application in noninvasive exhaled breath diagnosis of diabetes [3–5]. The acetone concentration in exhaled breath of diabetes is around 1800 ppb [6], therefore a rapid, real-time, and highly sensitive detection technique with low detection limit is urgently needed. Electronic gas sensors based on metal oxide semiconductors (MOSs) have been widely used for chemical vapor detection because of their high sensitivity, fast response speed, capacity for miniaturization and portability, as well as low cost, in comparison to gas or mass chromatography technologies [5,7,8]. Many nanostructured MOSs (such as ZnO [9–11], $TiO_2$ [12–14], $WO_3$ [15–17], $In_2O_3$ [18,19], and $Fe_2O_3$ [20,21]) have been investigated for gas sensing, among which $SnO_2$ has received the most attention as the sensing layer. $SnO_2$ has been commercially applied in MOSs gas sensors since 1970s and fundamental research has reported that it is able to respond to a variety of VOCs such as ethanol [22,23], acetone [24,25], n-butanol [26], formaldehyde [27], as well as $NO_2$ [28,29], CO [30], and $H_2$ [31,32]. However, the poor selectivity and low sensitivity of $SnO_2$ in detecting specific gases severely hinder its future development in breath diagnosis and wearable systems, which requires high selectivity and low limit of detection (LOD).

Fabrication of gas sensing layers with elaborated structures such as nanowires, nanotubes, nanosheets or porous hollow spheres have shown the advantage of selective detection of VOCs [33,34]. For example, $SnO_2$ nanofibers have been reported to have good selectivity to formaldehyde with a low temperature range of 120–150 °C [27], while nanoflowers are more selective to ethanol [22]. Very recently, Tonezzer reported that $SnO_2$ single crystalline nanowires are selective to $NO_2$ [35]. Although these nanostructures are possible to afford selectivity to some gases, they suffer from a relative low detection limit due to the low surface activity. Besides the nanostructure strategy, surface modification of MOSs by noble metals provides an alternative method to optimize the sensor properties *via* either electronic or catalytic sensitization [8,36–38]. Recently, Kim et al. synthesized Pt-loaded $SnO_2$ nanotubes for acetone sensing with a high response of 92 at 5 ppm [39]. Shao et al. reported Pd-doped $SnO_2$ thin film for acetone detection, which exhibits a short response time of 30 s at room temperature [40]. Jeong and co-workers synthesized $PtO_2$-loaded $SnO_2$ nanofibers, which achieves the high acetone response of 194.15 toward 5 ppm acetone [41]. However, the use of noble metals will increase the fabrication cost

* Corresponding authors at: College of Physics, Qingdao University, Qingdao 266071, China.
*E-mail addresses:* xianghong.liu@qdu.edu.cn (X. Liu), jun@qdu.edu.cn (J. Zhang).

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# Chemiresistive sensors based on core-shell ZnO@$TiO_2$ nanorods designed by atomic layer deposition for *n*-butanol detection

Yongshan Xu[a], Lingli Zheng[a], Chen Yang[a], Wei Zheng[a], Xianghong Liu[a,b,*], Jun Zhang[a,b,*]

[a] College of Physics, Qingdao University, Qingdao, 266071, China
[b] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin, 300071, China

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ABSTRACT

Constructing heterostructures with efficient modulation of electron transfer at the heterointerface affords great opportunity for electronic devices. Herein, a high performance nanosensor based on core-shell ZnO@$TiO_2$ nanorods is successfully realized for n-butanol detection. The n-n heterointerface formed between $TiO_2$ and ZnO allows for vast variation of conductivity due to electron confinement induced by their different works functions and enhances the response on exposure to gaseous molecules. Studies reveals that the shell thickness of $TiO_2$ has a great impact on the sensor performances, and the sensor based on ZnO@$TiO_2$ nanorods with 6.4 nm-thick $TiO_2$ shell delivers outstanding gas sensing properties in terms of high sensitivity, low detection limit (133 ppb), fast response-recovery, and excellent selectivity towards n-butanol detection. The mechanism for the improved gas sensing function is ascribed to the heterojunctions of core-shell nanostructure, the enhanced oxygen adsorption due to the $TiO_2$ shell and the fully electron-depleted $TiO_2$ shell layer with a thickness comparable to the Debye length. The strategy presented here is generally applicable and can provide some hints to design efficient electronic sensors with optimized performances.

## 1. Introduction

N-butanol, a colorless, irritating and narcotic liquid, is widely used in laboratories and factories as solvent, extracting agent and organic synthesis intermediates. Long time exposure in the environment of n-butanol could cause several symptoms like dermatitis, headache, dizzy and somnolence [1,2]. The National Institute for Occupational Safety and Health (NIOSH) has recommended an exposure limit of 50 ppm for safety concerns [3]. Therefore, efficient and accurate sensor technology for monitoring of ppm-level n-butanol is urgently needed.

Metal oxide semiconductors (MOSs) have demonstrated a great potential as the sensing layers in gas sensors for gaseous detection related to, such as air quality monitoring and noninvasive diagnosis benefiting from the advantages of easy synthesis, low production cost and tunable sensing performances [4–8]. However, low sensitivity, high operating temperature and poor selectivity currently remain the challenges that plagues the practical utilization of MOSs for nanosensors.

Nano-heterostructures have been widely used in gas sensors to acquire high sensitivity and favorable selectivity by virtue of the synergy of different material properties such as boosting catalytic activity, increasing adsorption sites and creating a charge carrier depletion layer that produces a larger modulation in resistance [8–13]. One-dimensional (1D) core-shell nanostructure are of particularly interest for fabrication of nanodevices, due to the maximized heterointerface, high specific surface area, and high carrier mobility along the 1D direction [8,14,15]. In addition, 1D core-shell nanostructure can afford a prominent electron confinement at the interface due to the different work functions of the core and the shell materials, thereby providing a big potential to explore the sensor functionality [16–20]. Our previous work revealed that core-shell α-$Fe_2O_3$@ZnO nanospindles had an excellent selectivity and high response to ethanol [12]. Furthermore, Kim and co-worker synthesized $SnO_2$-ZnO core-shell nanowires and revealed that the shell thickness of ZnO had a giant influence on the CO gas sensing performances [21]. Zhang et al. comparatively studied the sensor responses of $In_2O_3$-$SnO_2$ and $SnO_2$-$In_2O_3$ core-shell nanofibers and found that the former exhibited higher response to trimethylamine. The results indicates that the different work function in the heterostructure can lead to varied gas sensing performances [22]. Lu et al. reported p-CuO/n-$SnO_2$ core-shell nanowires for selective formaldehyde detection, which shows a response of 2.42–50 ppm formaldehyde at 250 °C [23].

Atomic layer deposition (ALD), based on the surface self-limiting reactions, is capable of growing thin films with high precision of atomic scale and the materials grown by ALD are conformably coupled to the

* Corresponding authors at: College of Physics, Qingdao University, Qingdao, 266071, China.
*E-mail addresses:* xianghong.liu@qdu.edu.cn (X. Liu), jun@qdu.edu.cn (J. Zhang).

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Research Article

# Oxygen Vacancies Enabled Porous $SnO_2$ Thin Films for Highly Sensitive Detection of Triethylamine at Room Temperature

Yongshan Xu, Lingli Zheng, Chen Yang, Wei Zheng, Xianghong Liu, and Jun Zhang*

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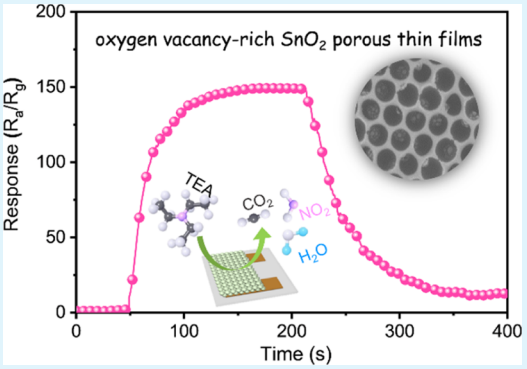
**ABSTRACT:** Detection of volatile organic compounds (VOCs) at room temperature (RT) currently remains a challenge for metal oxide semiconductor (MOS) gas sensors. Herein, for the first time, we report on the utilization of porous $SnO_2$ thin films for RT detection of VOCs by defect engineering of oxygen vacancies. The oxygen vacancies in the three-dimensional-ordered $SnO_2$ thin films, prepared by a colloidal template method, can be readily manipulated by thermal annealing at different temperatures. It is found that oxygen vacancies play an important role in the RT sensing performances, which successfully enables the sensor to respond to triethylamine (TEA) with an ultrahigh response, for example, 150.5−10 ppm TEA in a highly selective manner. In addition, the sensor based on oxygen vacancy-rich $SnO_2$ thin films delivers a fast response and recovery speed (53 and 120 s), which can be further shortened to 10 and 36 s by elevating the working temperature to 120 °C. Notably, a low detection limit of 110 ppb has been obtained at RT. The overall performances surpass most previous reports on TEA detection at RT. The outstanding sensing properties can be attributed to the porous structure with abundant oxygen vacancies, which can improve the adsorption of molecules. The oxygen vacancy engineering strategy and the on-chip fabrication of porous MOS thin film sensing layers deliver great potential for creating high-performance RT sensors.




**KEYWORDS:** *tin dioxide, porous film, oxygen vacancy, room temperature, gas sensor*



## 1. INTRODUCTION

Nowadays, the demand for real-time monitoring of ambient air quality has led to the rapid expansion of the gas sensor market.[1] Gas sensors are essential devices for gas leakage detection, public security, as well as medical diagnosis, and also play an indispensable role in future internet of things.[2,3] Among many types of gas sensors, metal oxide semiconductor (MOS)-based chemiresistive gas sensors are most attractive, benefiting from their merits such as simplicity, easy fabrication, low cost, and high sensitivity.[2,4−6] However, this type of sensor still significantly suffers from issues such as high energy consumption because of the high working temperature, and paramount research activities have been conducted to tackle these challenges.[7−9]

Generally, high-temperature operation is required by MOS gas sensors to overcome the energy barrier of sensing reactions.[10,11] The generation of more active oxygen species such as $O_2^-$ and $O^-$ on the MOS surface is highly related to the working temperature.[5,12] On the one hand, high-temperature operation greatly hampers their prospects for application, for example, in the detection of highly combustible and explosive gaseous targets. On the other hand, the high-temperature operation requires the use of a heater, which contributes to the cost and the complexity of the fabrication process. Therefore, room temperature (RT) gas sensors have acquired enormous interest.[2,13,14] Previous research has demonstrated that coupling carbon materials such as graphene and carbon nanotubes, or conducting polymers, to MOS can realize the RT response to $H_2S$,[15] $NO_2$,[16,17] $NH_3$,[18] and $H_2$.[19,20] Synthesis of heteronanostructures from multiple MOS or using noble metal catalysts to fabricate metal/oxide nanomaterials has also proved to be effective to obtain RT sensors.[21,22] Nevertheless, the detection of volatile organic compounds (VOCs) at RT using pristine MOS without using a catalyst to achieve high sensitivity and selectivity is still challenging.

Regulation of the electronic structure and the surface activity of MOS is the key to realize RT-sensing functions. Defect engineering has been utilized to optimize the surface activity

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