Novel Self-Assembly Route Assisted Ultra-Fast Trace Volatile Organic Compounds Gas Sensing Based on Three-Dimensional Opal Microspheres Composites for Diabetes Diagnosis

Tianshuang Wang, Sufang Zhang, Qi Yu, Siping Wang, Peng Sun, Huiying Lu, Fangmeng Liu, Xu Yan, and Geyu Lu

State Key Laboratory on Integrated Optoelectronics, Key Laboratory of Gas Sensors, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, Jilin Province, People’s Republic of China

ABSTRACT: The development of ultra-fast response semiconductor gas sensors for high-accuracy detection of trace volatile organic compounds in human exhaled breath still remains a challenge. Herein, we propose a novel self-assembly synthesis concept for preparing intricate three-dimensional (3D) opal porous (OP) SnO₂-ZnO hollow microspheres (HM), by employing sulfonated polystyrene (S-PS) spheres template-assisted ultrasonic spray pyrolysis. The high gas accessibility of the unique opal hollow structures resulted in the existence of 3D interconnection and bimodal (mesoscale and macroscale) pores, and the n–n heterojunction-induced change in oxygen adsorption. The 3D OP SnO₂-ZnO HM sensor exhibited high response and ultra-fast dynamic process (response time ∼4 s and recovery time ∼17 s) to 1.8 ppm acetone under highly humid ambient condition (98% relative humidity), and it could rapidly identify the states of the exhaled breath of healthy people and simulated diabetics. In addition, the rational structure design of the 3D OP SnO₂ HM enables the ultra-fast detection (within 1 s) of ethanol in simulation drunk driving testing. Our results obtained in this work provided not only a facile self-assembly approach to fabricate metal oxides with 3D OP HM structures but also a new methodology for achieving noninvasive real-time exhaled breath detection.

KEYWORDS: gas sensor, ultra-fast response, self-assembly method, 3D opal, diabetes diagnosis

1. INTRODUCTION

The breath analysis has obtained intensive attention in recent years because human exhaled breath contains multiple volatile organic compounds (VOCs) that can be used as key biomarker gases for disease diagnosis. Among the various breath analysis equipment, semiconductor metal oxide (SMO) sensors with miniaturization and integration features, high response, and real-time monitoring characteristic have been regarded as a potential candidate. Acetone (CH₃COCH₃) is a medically important gas, which is known as a biomarker for diabetes diagnosis, and the concentration of acetone has been reported to be higher than 1.8 ppm in the exhaled breath by diabetics. Thus, this demonstrates that the real-time diabetes diagnosis in a noninvasive and convenient manner by breath analysis is possible. In addition to disease diagnosis, the breath analysis also can be used in instantaneous detection of ppm level of ethanol (C₂H₅OH) in drivers’ exhaled breath, which is particularly important for urban traffic safety management. However, human exhaled breath contains saturated levels of water vapor [80% relative humidity (RH)] and over 1000 kinds of gas species; these can interfere with the accuracy of exhaled breath analysis. Accordingly, in order to meet the actual applications, it is more urgent to develop SMO gas sensors with high sensitivity, excellent selectivity, and rapid response that are impervious to humidity.

Oxide semiconductor chemiresistors with enhanced gas accessibility will be beneficial for accelerating the surface chemical reaction between the surface adsorbed oxygen and target gases. Therefore, a simple but effective performance improvement is to prepare the sensing materials with hollow microstructure (HM) based on the utility factor principle. As one of the ideal patterns for ordered porous structures, the opal microstructures assembled from multiple hollow nanospheres have intriguing properties, such as large specific surface area, low density, interstitial hollow spaces, and high diffusion coefficient, leading to their potential applications in the fields of photoelectrochemical water splitting, Raman scattering detection, and gas sensors. For the preparation of opal materials, numerous approaches have been developed based on spin coating, interfacial self-assembly, and dip coating. For instance, Su et al. fabricated Fe₂O₃ mono/multilayer hollow spheres array by the template-assisted hydrothermal method.
approach.22 Rao et al. prepared ordered metal oxide hollow sphere arrays through combining the chemical bath precipitation with the self-assembled PS sphere array template.26 However, time-consuming and sophisticated synthesis processes, expensive/bulky instrumentation equipment, and special surface treatment steps seriously hamper the large-scale and repeatable industrial production. Therefore, it is still important and of scientific significance for developing a facile strategy for the preparation of opal microstructures. In this regard, we proposed a straightforward self-assembled synthetic route relying on the ultrasonic spray pyrolysis (USP) method and the sulfonated polystyrene (S-PS) spheres template for the preparation of three-dimensional (3D) opal porous (OP) HM assembled from multiple hollow nanospheres. The high gas accessibility of this novel opal structure could provide more active surface sites, thus resulting in the high sensitivity and ultra-fast response/recovery speeds.9 Moreover, this synthetic route is also easy to control the size of opal microsphere and provide the multimodality of the pores.16,18,27

In this work, the 3D OP SnO2–ZnO HM was prepared via the novel self-assembled strategy combining the S-PS spheres template with the USP method. Interestingly, the as-prepared sample (single OP SnO2–ZnO HM) was assembled from multiple porous hollow SnO2–ZnO nanospheres (average diameter ≈200 nm). As expected, the 3D OP SnO2–ZnO HM had a highly ordered 3D opal hollow structure, bimodal porous system (sizes ≈9 and 60 nm), and abundant n–n heterointerfaces (SnO2, n-type, Eg = 3.6 eV; ZnO, n-type, Eg = 3.37 eV).14,28–30 More importantly, the 3D OP SnO2–ZnO HM sensor exhibited high sensitivity and ultra-fast response/recovery speeds to the exhaled breath of the simulated diabetics, with low interference from humidity, making them useful for early diabetes diagnosis. Furthermore, the 3D OP SnO2 HM sensor enabled the real-time monitoring of drunk driving. To the best of our knowledge, 3D opal hollow sensing materials prepared by a facile self-assembled method and used in breath analysis have never been reported before.

2. EXPERIMENTAL PROCEDURES

2.1. Material Synthesis. PS sphere powders were synthesized by an emulsion-free polymerization method,9 and then functionalized through sulfonation process for preparing the S-PS spheres (mean size: ~200 nm, Figure S1) that contained a hydrophilic outer layer with sulfonic acid (SO3H−) groups.31 Furthermore, Fourier transform infrared (FT-IR) spectroscopy was used to verify the transformation of PS spheres after sulfonation (Figure S2). The 3D OP SnO2–ZnO HM were prepared by the USP method and subsequent heat treatment. To prepare the ultrasonic spray solution, a certain amount of SnCl2·5H2O, a certain amount of ZnCl2, and 0.175 g S-PS sphere powders were dissolved in 15 mL deionized water, 0.3 mL hydrogen peroxide solution, and 0.16 mL of 0.2 M hydrochloric acid. The resulting solutions were stirred for 4 h at 25 °C. The Sn/Zn mole ratios were set as 1:0 (pure SnO2), 1:1, and 0:1 (pure ZnO), which were labeled as S1, S2, and S3, respectively. Besides, the solid SnO2 microspheres (S0 sample) were prepared without the S-PS sphere template. The detailed preparing process and schematic of the experimental setup used for the USP are shown in Figure S3. The precipitate was separated by centrifugation, washed with deionized water, and then dried in air. Finally, the as-prepared precursors were calcined at 600 °C for 3 h.

2.2. Characterization of the Gas-Sensing Properties. The gas sensor device and synthesis process are illustrated in Figure S4. The gas-sensing properties were measured by a static testing system.14 The gas response was defined as Rgas/Rair (for reducing gases, e.g., CH3OH, C7H8, C3H6O, etc.). Response (τres) and recovery (τrec) times were defined as the times required to reach 90% of the total resistance change in the tested gas and air. In the case of the simulated diabetics exhaled breath analysis, we gathered the exhaled breaths of 7 healthy volunteers (all volunteers were fasting 5 h) using a Tedlar bag (Figure S5); the mixing gas consisted of exhaled breath and 1.8 ppm aceton as simulated diabetics exhaled breath. Moreover, in the case of the simulated drunk driving testing, we gathered three kinds of testing samples (denoted as T1, T2, and T3), where T1 was the exhaled breath of one healthy person before drinking beer, T2 was the exhaled breath of this person after 30 min of drinking one cup of beer, and T3 was the exhaled breath of this person after 30 min of drinking one cup of beer. The specific parameters of one cup of beer were as follows: alcohol content of beer ≥3.6 vol % and the volume of one cup ~355 mL. Finally, the samples were injected into the sensing measurement system using a diaphragm pump.

3. RESULTS AND DISCUSSION

3.1. Material Characterization. Schematic illustration for the preparation of 3D OP porous HM is shown in Scheme 1. During the synthesis process, the hydrochloric acid (0.2 M) was added to control the pH value; tin(IV) chloride pentahydrate and zinc chloride can gently release the Sn4+ and Zn2+ during hydrolysis, thus forming the S-PS sphere/tin hydroxide/zinc hydroxide composite colloids.32 The solution containing the S-PS sphere/tin hydroxide/zinc hydroxide composite colloids is nebulized by ultrasonic spray and inert gas (N2) as a carrier gas. Detailed processes are as follows: route 1: (1) Pyrolysis at ~200 °C in N2; 3D self-assembly of the composite colloids (assembled into highly ordered 3D opal...
precursor), solvent evaporation, and metal particles adhere to the surface of S-PS spheres. Route 2: (1) Pyrolysis at \( \sim 700^\circ C \) in N\(_2\) and the 3D opal microstructured composites converted into carbon/tin hybrid/zinc hybrid by carbonization at 700 \(^\circ C \) in N\(_2\). Through the carbonization of the templates, highly ordered microstructures can be effectively protected, and frame collapse at high temperatures can be avoided. (2) Heat treatment at \( \sim 600^\circ C \) in air and 3D OP SnO\(_2\)−ZnO HM obtained after removing carbon species. Finally, the bimodal porous system (macroscale pores \( \sim 60 \text{ nm} \) and mesoscale pores \( \sim 9 \text{ nm} \)) could be formed in 3D opal microstructures, which effectively improved the utility factor (larger specific surface area).

X-ray diffraction (XRD) pattern of the S1 sample (3D OP SnO\(_2\) HM) could be well indexed to the tetragonal structure of SnO\(_2\) (JCPDS card 41-1445) (Figure 1a). The S2 sample (3D OP SnO\(_2\)−ZnO HM) had two crystalline phases of the tetragonal SnO\(_2\) and the wurtzite hexagonal ZnO (JCPDS card 36-1451) simultaneously (Figure 1a). Besides, it could be observed that the intensity of the ZnO diffraction peaks was reduced and the full width at half maximum of ZnO became narrow, indicating that some Sn could be incorporated into the lattice of ZnO and the incorporation of Sn resulted in the increase in the particle size of ZnO crystallites. XR pattern of the S3 sample (3D OP ZnO HM) showed the wurtzite hexagonal structure of ZnO (Figure 1a). In addition, the crystallite sizes of the SnO\(_2\) and ZnO crystallites in 3D OP SnO\(_2\), SnO\(_2\)−ZnO, and ZnO HM were calculated from XRD pattern using Scherrer’s equation (Table S1). The morphology of the 3D OP SnO\(_2\)−ZnO HM (S2 sample) was a highly ordered 3D opal microsphere framework that assembled from multiple hollow porous nanospheres (Figure 1b). The mesopores (2−10 nm, red dotted circles) and macropores (>50 nm, yellow arrows) could be clearly observed on the surfaces of 3D OP SnO\(_2\)−ZnO HM (Figure 1c). Besides, the diameter of the single hollow porous SnO\(_2\)−ZnO nanosphere (\( \sim 200 \text{ nm} \)) was similar to that of the removed S-PS sphere. The S1 and S3 samples also had 3D OP HM skeletons (Figure S6). As shown in the scanning electron microscopy (SEM) image (Figure 1d) of the solid SnO\(_2\) microspheres (the detailed synthetic process of solid SnO\(_2\) microspheres in the Experimental Procedures), the microsphere had a clean surface.
and dense inner structure because of the absence of the S-PS sphere template. The size distribution of the S2 sample is shown in a histogram (Figure 1e) by analyzing 100 microspheres. It can be found that the S2 sample had a narrow size distribution (diameter range: 545−1255 nm, mean diameter: ∼818 nm). The 3D OP HM morphology of the S2 sample was homogeneous (Figure 1f).

The inner structure of the 3D OP SnO2−ZnO HM was further confirmed by transmission electron microscopy (TEM) analysis. The TEM image could further indicate that the single 3D OP HM were assembled from multiple hollow porous nanospheres, and the rule of each hollow porous nanosphere is connected in an orderly way (Figure 2b). The results indicated that the diameter of the S-PS sphere still remained, and each hollow nanosphere did not collapse after removing the S-PS sphere and decomposing the precursor. Figure 2c further showed potent evidence that the single 3D OP HM was composed of multiple hollow porous nanospheres. The S1 and S3 samples also had 3D OP HM microstructures (Figure S7a,d), indicating that the microstructure will not be changed with the introduction of another metal oxide. The clear lattice fringes with an interplanar spacing of 1.77 and 3.34 Å are attributed to the (211) and (110) plane of the tetragonal phase SnO2 (Figure 2e).38 Also, the existence of lattice fringes (1.92 Å) can be attributed to the (102) wurtzite hexagonal plane of ZnO.39 Furthermore, the lattice planes of ZnO (002), SnO2 (110), SnO2 (211), and SnO2 (112) were identified in the SAED pattern of the S2 sample (Figure 2a).30 The crystallographic structures and corresponding SAED patterns of the S1 and S3 samples are exhibited in Figure S7b,c,e,f. Figure 2d displays the corresponding elemental spacial distribution of the individual S2 sample. In addition, elemental mapping of the S2 sample indicated that all the elements (Sn, Zn, and O) were homogeneously distributed over the entire 3D OP HM (Figure 2d).

Figure 3. (a) N2 adsorption/desorption isotherms of the S0 and S2 samples, and the corresponding specific surface areas and pore size distributions of the (b,d) S2 and (c,e) S0 samples.

Figure 4. Gas responses of (a) S1, (c) S2, and (e) S3 sensors to 100 ppm of different tested gases at discrepant operating temperatures, and dynamic response/recovery curves of (b) S1 sensor to ethanol in the range 1−800 ppm at 250 °C, (d) S2 sensor to acetone in the range 0.25−100 ppm at 275 °C, and (f) S3 sensor to acetone in the range 5−100 ppm at 350 °C. (g) Schematic diagram showing the structure of the 3D OP SnO2−ZnO HM.
2d). The X-ray photoelectron spectroscopy (XPS) analysis of the S2 sample is exhibited in Figure S8. The binding energies of the Sn 3d_{5/2} and Sn 3d_{3/2} peaks in XPS (Figure S8b) were 486.6 and 495.1 eV, respectively.30 The peaks appearing in Figure S8c centered at 1021.4 and 1044.5 eV were attributed to the Zn 2p_{3/2} and Zn 2p_{1/2} respectively.18 Also, the XPS peaks of O 1s can be fitted into three kinds of oxygen species (Figure S8d).14

The pore size distribution and specific surface areas of the specimens were measured from the N2 adsorption/desorption isotherm (Figures 3 and S9). As shown in Figure 3a, the N2 adsorption/desorption isotherms of the S2 sample were between the type II and type IV Brunauer isotherm with a H3 hysteresis loops, indicating the presence of mesopores, whereas the S0 sample (see the detailed synthetic process in the Experimental Procedures) showed a type II Brunauer isotherm, which was typical for non-porous structures.16 The Brunauer–Emmett–Teller specific surface areas of the S0 and S2 specimens were 2.9 and 8.81 m² g⁻¹, respectively (Figure 3b,c). The specific surface area increased significantly with the introduction of the S-PS sphere template, suggesting that the opal, porous, and hollow structure can render both surface and inner side chemical reactions.9 Pores with the diameter of ~9 nm were found in the S2 sample (Figure 3d), which was generated by outgassing during the S-PS template decomposing.17 Pores with the diameter of ~60 nm were also observed in the S2 sample, which came from some broken porous hollow nanospheres during calcination process.40 There were no significant pores in the S0 sample (Figure 3e). Combining the advantages of the porous system (bimodal pores: meso- and macroscale pores) and the larger specific surface area, 3D OP HM achieved a higher response toward the target gas.9

### 3.2. Gas-Sensing Characteristics

High selectivity and response toward the target gas is quite an important functional character for gas sensors. Therefore, the gas responses of the S1, S2, and S3 sensors to 100 ppm of different tested gases at discrepant operating temperature were investigated. As shown in Figure 4a, when operating at 250 °C, the response of the 3D OP SnO2 HM (S1) sensor to 100 ppm ethanol (R_{air}/R_{gas} = 21.8) was ~1.73 times higher than that to acetone (R_{air}/R_{gas} = 12.6); when operating at higher temperature (275 °C), the response of the S1 sensor to 100 ppm acetone (R_{air}/R_{gas} = 11.9) was ~1.19 times higher than that to ethanol (R_{air}/R_{gas} = 10), indicating that the S1 sensor is suitable for monitoring ethanol at 250 °C. In contrast, as shown in Figure 4c, the S2 and S3 sensors revealed the highest response to acetone (S2: R_{air}/R_{gas} = 45.8 and S3: R_{air}/R_{gas} = 17.2) at a higher operating temperature (S2: 275 °C and S3: 350 °C). However, when reducing the operating temperature of the S2 (250 °C) and S3 (325 °C) sensors, the responses to ethanol and acetone became similar or comparable. Therefore, the change in gas selectivity can be discussed with respect to the changes in gas accessibility, surface reactivity, and charge carrier concentration because of the formation of heterostructure composites.41 Furthermore, the lowest unoccupied molecule orbit energy for gas molecule and the operating temperature also influenced the selectivity.42,43

Dynamic response and recovery curves in Figure 4b pointed to the fact that the S1 sensor had good response/recovery features, with its response increasing with increasing ethanol concentrations from 1 to 800 ppm. Besides, the S1 sensor response versus ethanol concentration (1–800 ppm) is investigated in Figure S10a. These results demonstrated that the S1 sensor can detect ethanol at a wide concentration range, and the response–concentration plot of the S1 sensor showed a good linearity. Figure 4d,f exhibited the dynamic acetone-sensing characteristics of the S2 and S3 sensors at a concentration range of 0.25–100 ppm (275 °C) and 5–100 ppm (350 °C), respectively. A 2.67-fold enhanced acetone sensitivity (R_{air}/R_{gas} = 45.8 at 100 ppm) was observed with the S2 sensor when compared with that of the S3 sensor (R_{air}/R_{gas} = 17.1 at 100 ppm). The S2 and S3 sensors exhibited excellent reproducible characteristics in the studied range. Furthermore, the single 3D OP microsphere assembled from multiple hollow nanospheres enabled more acetone molecules to diffuse over the entire sensing surface (Figure 4g). The limit of detection (LOD) of the S2 and S3 sensors toward acetone was 50 ppb and 5 ppm, respectively. The LOD of the S2 sensor was lower than the concentration level of 1.8 ppm in the diabetes patients’ breath.3 Besides, the S2 and S3 sensors both exhibited a good response–concentration relationship (Figure S10b,c).

Figure S11a–c shows the dynamic resistance transients of the S1–S3 sensors when exposed to 100 ppm target gas at their respective optimum operating temperatures. All sensors can quickly respond to the target gas and return to the baseline upon exposure to air.14 On the basis of Figure S11a–c, the response times of these three sensors were all ~1 s because of the enhancement in gas accessibility of the 3D OP hollow structure. Besides, the baseline resistance in air (R_{air}) was also measured for each sensor (Figure S12), indicating that the R_{air} value for pure SnO2 and ZnO sensors is significantly lower than that for the SnO2–ZnO sensor; it is attributed to the formation of n−n heterojunction between the interface of SnO2 and ZnO that increases the sensor resistance.44 Eight times repetitive sensing transients toward 100 ppm of acetone indicated the reproducibility of the S2 sensor (Figure S13).

Furthermore, the sensor exhibited relatively good stability over 20 days (Figure S14). As we all know, human exhaled breath contains saturated levels of water vapor (80 RH %), which is the interference factor in exhaled breath analysis application.3 Therefore, the dynamic gas-sensing transients of S2 sensor to 1.8 ppm acetone at 275 °C in dry (5 RH %) and humid (20, 40, 60, 80, and 98 RH %) atmospheres are investigated in Figure S15a,b. The 1.8 ppm acetone sensitivity of the S2 sensor was less affected by humidity. The resistance in air slightly decreased with increasing humidity, which showed a matched tendency with previous study and could be explained by the reported theory.44 Accordingly, the overall gas-sensing characteristics, such as R_{air}/R_{gas} (S), τ_{res} and τ_{reco} of the S2 sensor in dry (5 RH %) and humid (20, 40, 60, 80, and 98 RH %) atmospheres are summarized in Figure S15c,d. The S2 sensor shows relatively high response time(R_{air}/R_{gas} = 4.93 in dry and R_{air}/R_{gas} = 3.05 in 98 RH %), short response time (τ_{res} = 1 s in dry and τ_{res} = 4 s in 98 RH %), and short recovery time (τ_{reco} = 7 s in dry and τ_{reco} = 17 s at 98 RH %) (τ_{res} and τ_{reco} the times to reach 90% resistance change upon exposure to target gas and air, respectively). The τ_{res} and τ_{reco} of the S2 sensor exhibited little fluctuation with increasing humidity. Clearly, the gas response decreased with the increase in RH.3 To quantify the humidity dependence of the gas-sensing characteristics, we calculated the ratios of the gas responses (S_{water}/S_{air RH%}) and the resistances in air (R_{air-water}/R_{air-20 RH%}) (Figure S16). S_{water}/S_{air RH%} = 1 and R_{air-water}/R_{air-20 RH%} = 1 mean that there was no observed humidity dependence. The S2 sensors showed high S_{water}/S_{air RH%} values (0.9, 0.86, 0.8, and 0.75 in 40, 60, 80, and 98 RH
%, respectively) and high $R_{\text{air-wet}}/R_{\text{air-20 RH\%}}$ values (0.9, 0.87, 0.82, and 0.76 in 40, 60, 80, and 98 RH %, respectively). These results clearly suggested that the S2 sensor can detect acetone with a high response, rapid response/recovery speed, and negligible humidity interference. In this study, the gas sensor based on the 3D OP SnO$_2$–ZnO HM clearly demonstrates significantly ultra-fast response/recovery speed toward very low concentrations of acetone at lower operating temperature.

Figure 5. (a) The identification of human exhaled breath (healthy subjects and simulated diabetics) based on S2 sensor, (b) dynamic resistance change transients of the S2 sensor to human exhaled breath (healthy subjects and simulated diabetics), (c) the identification of human exhaled breath (sober subjects and simulated drunk driving driver) based on S1 sensor, and (d) dynamic resistance change transients of S1 sensor to human exhaled breath (sober subjects and simulated drunk driving driver).

Figure 6. (a,b) Schematic illustration of the sensing mechanism of the 3D OP SnO$_2$–ZnO HM sensor, and (c,d) schematic illustration for the formation of an opal porous hollow structure.
in ambient conditions at 98% RH when compared to previous reports (Table S2).

In order to further verify the potential application value of the 3D OP SnO$_2$–ZnO HM gas sensor, the simulation test was carried out by distinguishing the exhaled breath of healthy people from the simulated diabetes breath (the healthy exhaled breath mixed with 1.8 ppm of acetone; the synthesis process is listed in the Experimental Procedures). The concentration of acetone was fixed to 1.8 ppm because the diabetes patients’ breath contains more than 1.8 ppm of acetone in exhaled breath. The response values (~2.64) of the S2 sensor became approximately twofold higher than those of a healthy person’s exhaled breath, and the difference in response between diabetic and healthy volunteers became more obvious. The dynamic gas-sensing transients of the S2 sensor to healthy subjects and simulated diabetes subjects at 275 °C are shown in Figure 5b; it could be found that the S2 sensor still had ultra-fast response and recovery speeds in actual application. Moreover, the 3D OP SnO$_2$ sensor (S1) was applied to detect ethanol in exhaled breath; we carried out exhaled breath analysis using T1, T2, and T3 testing samples (see the detailed synthetic process of simulated exhaled breath in the Experimental Procedures). From the point of view of human blood alcohol concentration, normal people drink one cup (300 mL) of beer, and the blood alcohol concentration can reach the drunk driving standard (20 mg/100 mL) after 10 min. The drunk driving samples (S$_T$ = 6.3 and S$_T$ = 6.1) were accurately distinguished from normal breath samples (S$_T$ = 2.7) by using S1 sensor (Figure 5c). These results further confirmed the excellent capabilities of the 3D OP HM sensor in achieving accurate and rapid detection and identification of VOCs in exhaled breath.

According to the fundamental chemical-sensing theory, SMOs identify reducing gases through a change in resistance caused by the reaction between chemisorbed oxygens (O$_2$, O$_{chem}$, and O$_{ads}$) and targeted gas molecules. In this study, the high sensitivity of 3D OP SnO$_2$–ZnO HM toward acetone is ascribed to several factors. On one hand, the formation of n–n heterojunction in 3D OP SnO$_2$–ZnO HM enhanced sensing properties. The energy band structure of SnO$_2$–ZnO heterojunction can be seen in Figure 6a,b. It is known that the work functions of SnO$_2$ and ZnO are 4.55 and 5.20 eV, respectively. The SnO$_2$ and ZnO band edge positions are predicted to determine the migration directions of the carriers. where $X$ is the absolute electronegativity of the semiconductor, $E^*$ is the energy of free electrons on the hydrogen scale (~4.5 eV), and $E_g$ is the band gap of the semiconductor. Also, the predicted band edge positions of SnO$_2$ and ZnO are exhibited in Table S3. Initially, when SnO$_2$ and ZnO nanoparticles come into contact, the recombination between the electron in SnO$_2$ and the hole in ZnO occurs, until equilibrium in terms of Fermi levels is reached, and the recombination causes the formation of depletion layer at the interface (Figure 6b). Because of the electric potential changes in the space charge region, the energy band on the side of SnO$_2$ is bent upward by 0.18 eV, and the energy band on the side of ZnO is bent downward by 0.47 eV. The heterojunction structure will lead to the considerable change in the thickness of electron depletion regions, resulting in a significantly sensitive resistance variation when exposed to acetone (Figure 6c,d). On the other hand, the unique opal hollow structure had a continuous structured skeleton, 3D interconnection bimodality pore system, excellent channels, and high gas accessibility (Figure 6c,d). Thus, the 3D OP HM sensors possessed higher response and ultra-fast response/recovery speeds. For confirmation of the important role of improving the utility factor of the sensing materials, additional sensing measurements were carried out between the S0 (the solid SnO$_2$ microspheres mentioned in the Experimental Procedures) and the S1 (the 3D OP SnO$_2$ HM) sensors (Figure S17); the S1 sensor showed a higher response at lower operating temperature than the S0 sensor. Note that most of the key parameters (the size of 3D opal microsphere, the size of pore, and sensing material components) can be separately controlled by manipulating the self-assembly sacrificial S-PS templates, the metal oxides, the pyrolysis temperature, and the flow rate of carrier gas. The synthetic route developed in this study can be used as a powerful tool to design high-performance gas sensors.

4. CONCLUSIONS

In summary, the USP of droplets containing multiple metal precursors combined with the S-PS spheres was developed as a straightforward self-assembly synthetic route for the preparation of highly ordered 3D OP SnO$_2$–ZnO HM. This novel opal microstructure was assembled from multiple porous hollow nanospheres (average diameter of 200 nm), and had bimodal pores (pore sizes ≈9 and 60 nm), which could facilitate gas diffusion into sensing layers. As expected, the 3D OP SnO$_2$–ZnO HM sensor showed high response, ultra-fast response/recovery speeds, and remarkable stability to acetone at 275 °C. More importantly, the 3D OP SnO$_2$–ZnO HM sensor successfully distinguished the 7 simulated diabetic breaths and 7 healthy people breaths. In addition, the breath alcohol testing sensor using 3D OP SnO$_2$ HM sensor resulted in clear discrimination of the simulation drunk driving volunteer in a short time (1 s). The results presented herein can bring a new generation and an effective way for the design and self-assembly of high-quality metal oxide nanostructures in the field of real-time health care monitoring and timely drunk driving testing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b13010.

SEM images of the S-PS spheres, the S1 sample and the S3 samples; FT-IR spectra of PS and S-PS spheres; schematic diagrams of the USP setup and the gas sensor device; the way to collect the exhaled breath into a Tedlar bag and the exhaled breath sample; TEM and HR-TEM images, and SAED patterns of S1 and S3
samples; XPS spectra of S2 sample; and gas responses of the sensors (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: pengsun@jlu.edu.cn (P.S.).

*E-mail: lugy@jlu.edu.cn (G.L.).

**ORCID**

Peng Sun: 0000-0002-9509-9431

Xu Yan: 0000-0003-2152-675X

Geyu Lu: 0000-0002-7428-2456

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by the National Key Research and Development Program of China (no. 2016YFC0207300), National Nature Science Foundation of China (no. 61771365, 61703039, 61527804), National High-Tech Research and Development Program of China (863 Program, no. 2014AA06A505), Science and Technology Development Program of Jilin Province (no. 201705206251), the Program for JLU Science and Technology Innovative Research Team "JLUST-TIRT", and the Fundamental Research Funds for the Central Universities.

**REFERENCES**


(51) Bai, S.; Liu, H.; Luo, R.; Chen, A.; Li, D. SnO2@Co3O4-p-n heterostructures fabricated by electrospinning and mechanism analysis enhanced acetone sensing. *RSC Adv.* 2014, 4, 62862–62868.
