Hierarchical highly ordered SnO$_2$ nanobowl branched ZnO nanowires for ultrasensitive and selective hydrogen sulfide gas sensing

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**Abstract**

Highly sensitive and selective hydrogen sulfide (H$_2$S) sensors based on hierarchical highly ordered SnO$_2$ nanobowl branched ZnO nanowires (NWs) were synthesized via a sequential process combining hard template processing, atomic-layer deposition, and hydrothermal processing. The hierarchical sensing materials were prepared in situ on microelectromechanical systems, which are expected to achieve high-performance gas sensors with superior sensitivity, long-term stability and repeatability, as well as low power consumption. Specifically, the hierarchical nanobowl SnO$_2$@ZnO NW sensor displayed a high sensitivity of 6.24, a fast response and recovery speed (i.e., 14 s and 39 s, respectively), and an excellent selectivity when detecting 1 ppm H$_2$S at 250 °C, whose rate of resistance change (i.e., 5.24) is 2.6 times higher than that of the pristine SnO$_2$ nanobowl sensor. The improved sensing performance could be attributed to the increased specific surface area, the formation of heterojunctions and homojunctions, as well as the additional reaction between ZnO and H$_2$S, which were confirmed by electrochemical characterization and band alignment analysis. Moreover, the well-structured hierarchical sensors maintained stable performance after a month, suggesting excellent stability and repeatability. In summary, such well-designed hierarchical highly ordered nanobowl SnO$_2$@ZnO NW gas sensors demonstrate favorable potential for enhanced sensitive and selective H$_2$S detection with long-term stability and repeatability.

**Introduction**

Hydrogen sulfide (H$_2$S), one of the most dangerous hazardous gases, has aroused widespread concern for its severe toxicity to the human body as well as being normally generated from industries. Trace levels of H$_2$S are sufficient to damage the human respiratory system as well as cause unconsciousness neurological sequelae and cardiovascular-related death. In view of this, it is of great significance to effectively detect and monitor H$_2$S in the surrounding living environment. To date, diverse chemical sensors based on different mechanisms have been extensively investigated and developed to detect trace levels of H$_2$S, including chemiresistive, electrochemical, and optical sensors. Among these, semiconducting metal oxide (SMO)-based chemiresistive sensors have attracted tremendous research interest due to their irreplaceable advantages of low cost, convenient fabrication, and great integrated circuit compatibility.

Among various investigated SMOs, tin-oxide (SnO$_2$) nanomaterials with different morphologies, such as nanoparticles, nanowires (NWs), nanofibers, and nanobamboos, have been intensively explored and regarded as the most promising candidates for high-performance gas sensors, with numerous merits, such as high carrier mobility, great chemical and thermal stability, and low cost. However, these nanostructures are...
Usually brush printed or drop coated onto ceramic tubes or microelectromechanical system (MEMS) devices, which intrinsically limits the reliability and repeatability of the fabricated sensors. Therefore, a new strategy of seamlessly integrating nanomaterials and microhotplate forms for the sensor fabrication process is of vital importance for obtaining high-performance gas sensors with excellent stability and repeatability, as well as low power consumption. Very recently, a hard template method was developed for in situ monolayer macroporous material synthesis, which fits the requirements mentioned above. The in situ preparation process could not only benefit wafer-level fabrication but also effectively reduce the contact resistance and improve the device performance. For instance, Gu et al. prepared an ordered macroporous structure of SnO2 by employing a monolayer polymethyl methacrylate (PMMA) sphere template, which exhibited excellent repeatability with ethanol and had a promising application in ethanol detection. Additionally, such a highly ordered monolayer macroporous structure demonstrated enhanced gas response and response speed due to its large specific surface area and well-interconnected pore structure.

However, pristine SnO2 gas sensors usually suffer from problems such as poor selectivity and long response-recovery time. Accordingly, diverse effective approaches have been developed to improve the performance of gas sensors, such as noble metal doping, hierarchical structure construction, and composite heterostructure design. In particular, the construction of hierarchical structures is beneficial for increasing the specific surface area and forming more nanojunctions at the interface between the initial and secondary nanostructures and has been widely regarded as one of the most promising strategies and has stimulated great research interest. For example, Alenezi et al. synthesized hierarchical zinc oxide (ZnO) NWs and nanodisks assembled from initial ZnO nanostructures following a hydrothermal process and demonstrated an enhancement in the acetone sensing performance in comparison to the initial ZnO monomorphological nanostructures. Furthermore, heterogeneous-hierarchical nanocomposites exhibited superior gas sensing performance than homohierarchical nanostructures considering the synergistic effect of various properties from different materials. Zhang et al. successfully synthesized novel brush-like SnO2@ZnO hierarchical nanostructures with SnO2 NW backbones and ZnO nanorod branches via a simple two-step hydrothermal method and demonstrated that the nitrogen dioxide (NO2) sensing performance of SnO2@ZnO hierarchical structures was substantially enhanced at a relatively low operating temperature (150 °C) in comparison to that of pristine ZnO and SnO2.

Herein, a novel synthetic route for the large-scale fabrication of hierarchical highly ordered SnO2 nanobowl branched ZnO NWs with excellent H2S sensing performance is proposed combining a hard template method for the preparation of highly ordered SnO2 nanobowl atomic-layer-deposition (ALD) processing of nanoscale ZnO seed layers on the surface of SnO2 nanobows, and modified hydrothermal processing for the growth of branched ZnO NWs. In particular, the ALD technique can precisely control the film thickness and provide uniform conformal coverage of ZnO seed layers on SnO2 nanobowls. The morphology of the hierarchical structures was tuned by the thickness of the ALD-controlled seed layers and the hydrothermal growth time. The hierarchical branches grown on highly ordered nanobowls can provide an enlarged specific surface area for gas adsorption, as well as efficient channels for electron transport, compared to that of the ZnO film shell. More importantly, hierarchical sensing materials were synthesized in situ on MEMS devices, which are expected to be high-performance gas sensors with superior sensitivity, long-term stability and repeatability, as well as low power consumption. As a result, the substantially enhanced sensing performance of hierarchical nanobowl SnO2@ZnO NW gas sensors to H2S compared to the pristine SnO2 nanobowl sensor and the heterostructured nanobowl SnO2@ZnO film sensor was demonstrated. Specifically, the hierarchical nanobowl SnO2@ZnO NW sensor displayed a high sensitivity \( \left( \frac{R_s}{R_g} \right) \) of 6.24, a fast response and recovery speed (i.e., 14 s and 39 s, respectively), and an excellent selectivity when detecting 1 ppm H2S at 250 °C, and its rate of resistance change (i.e., 5.24) is 2.6 times higher than that of the pristine SnO2 nanobowl sensor. The mechanisms of substantially improved sensing performance were proven by both electrochemical characterization and band alignment analysis, suggesting the synergistic effect of the hierarchical heterostructures, including increased specific surface area, the formation of heterojunctions and homojunctions, as well as the additional reaction between ZnO and H2S. Moreover, the well-structured hierarchical sensors maintained stable performance after a month, suggesting great stability and repeatability. The combined diversity of hierarchical heterogeneous nanocomposites with low-power MEMS holds favorable potential for highly sensitive and selective H2S gas sensors with long-term stability and repeatability.

**Results and discussion**

Figure 1a illustrates the synthetic protocol of the hierarchical highly ordered nanobowl SnO2@ZnO NWs in situ on MEMS combined with the ALD process. First, highly ordered monolayer polystyrene (PS) spheres soaked with SnCl4 precursor solution were obtained on
the MEMS substrate via a simple picking-up process. After thorough drying at room temperature and calcination in a muffle furnace at 550 °C for 2 h, the organic PS spheres were removed, and a uniform and shiny highly ordered SnO$_2$ nanobowl film could be seen on the surface of the MEMS substrate. Figure 1b, c and Fig. S1 show the optical microscopy and SEM images of the MEMS substrate with the obtained materials, displaying the whole structure of the MEMS gas sensor as well as demonstrating the intactness of the device after 550 °C calcination. Figure 2a shows the top-view SEM image of a randomly selected area of the SnO$_2$ nanobowl film, confirming that the film is composed of highly ordered SnO$_2$ nanobowls with a diameter of ~700 nm. It is noteworthy that the diameter of the nanobowls is slightly shorter than the diameter of the PS template, which reveals that the SnCl$_4$ precursor solution level was lower than the half height of the PS sphere. Moreover, since the PS spheres were closely packed on the substrate, an approximate triangular space was naturally formed among three adjacent spheres, exhibiting hexagonal close packing. Then, these highly ordered SnO$_2$ nanobowls were conformably coated by ZnO seed layers with different thicknesses through thermal ALD at 200 °C. The displayed SEM image in Fig. 2b indicates the as-prepared highly ordered nanobowl SnO$_2$@ZnO film morphology with a uniform and conformal ZnO seed layer. The average thickness of the ZnO seed layer turned out to be 20 nm with 100 ALD growth cycles, which is consistent with the result of the ZnO film grown on the flat Si wafer measured by the SE.
system. In addition, the thicknesses of the ZnO films with 50 and 150 ALD growth cycles were measured to be 10 and 30 nm, respectively. Evidently, the thickness of the ZnO film shows a continuous increase with a slope of ~0.2 nm/cycle when increasing the total ALD growth cycles. The corresponding samples are denoted as S@ZX in this work, where X = 0, 10, 20, and 30, representing the thicknesses of the ZnO films. Finally, owing to the uniform and conformal coverage of the ZnO seed layer, the ZnO NWs were successfully grown on the surface of the S@Z20 structure via a modified hydrothermal reaction. The ZnO NWs grew densely on the surface of S@Z20, with the highly ordered nanobowl morphology of S@Z20 remaining, appearing similar to a nest-like array (Fig. 2c). The optimal hydrothermal reaction time was further investigated to obtain hierarchical highly ordered nanobowl SnO2@ZnO NWs with an excellent morphology, which have as large a specific surface area as possible on the basis of maintaining a complete hierarchical structure. Similarly, the corresponding hierarchical samples are denoted as S@Z20-ZY, where Y = 1, 3, 5, and 8, representing the hydrothermal reaction time.

The morphologies of S@Z20-ZY (Y = 1, 3, 5, and 8) displayed regular changes with an increase in hydrothermal reaction time. At 1 h (Fig. 2d), the branched ZnO NWs were relatively short, and overall, the hierarchical S@Z20-Z1 retained a macroporous morphology. As shown in Fig. 2d, e and Fig. 2c, when the hydrothermal reaction time is increased from 1 to 5 h (i.e., S@Z20-Z1, S@Z20-Z3, and S@Z20-Z5), the length of branched ZnO NWs is significantly increased, and the whole hierarchical structure seems to be denser. As the hydrothermal reaction time reached 5 h, sample S@Z20-Z5 achieved a maximum length of branched ZnO NWs and maintained a complete hierarchical highly ordered nanobowl branched nanowire structure (Fig. 2c). However, when the hydrothermal reaction time further increased to 8 h, as shown in Fig. 2f, the SnO2 nanobowls were fully filled with ZnO NWs, which damaged the designed morphology and greatly limited the effective function of SnO2 nanobowls. In addition, the crystalline grain of ZnO NWs showed a significant increase (Fig. 2f), reducing the specific surface area. As a result, the optimal hydrothermal reaction time for branched ZnO NWs growing on highly ordered SnO2 nanobowls is 5 h.

Moreover, the effect of the seed layer thickness on the hierarchical nanowire-branched nanobowl structure was further investigated with a determined hydrothermal reaction time of 5 h. Figure 2g-i displays the morphologies of the samples S@Z0-Z5, S@Z10-Z5, and S@Z30-Z5. When the highly ordered SnO2 nanobowls without a ZnO seed layer were treated with a 5 h hydrothermal process,
branched ZnO NWs could not grow on the surface of the nanobowls, and instead, there would only be nanowires with large grain sizes physically adsorbed on the surface of S@Z20-Z5 across several nanobowls (Fig. 2g). Hence, a uniform and conformal seed layer deposited by ALD is of vital importance to the synthesis of hierarchical structures with branched nanowires. In addition, the thickness of the seed layer would specifically affect the entire hierarchical morphology. It was demonstrated that the highly ordered SnO2 nanobowls coated with a moderate-thickness ZnO seed layer (i.e., S@Z20-Z5) exhibited the optimal hierarchical structure (Fig. 2c). However, if the seed layer was much thinner (i.e., S@Z10-Z5), there would only be ZnO nanograins on the surface of the seed layer, which were not able to grow into nanowires (Fig. 2h). On the other hand, if the seed layer was too thick (i.e., S@Z30-Z5), the branched ZnO NWs grown via the 5 h hydrothermal process would completely fill the nanobowls, thus destroying the designed hierarchical structure (Fig. 2i).

The well-defined hierarchical nanowire-branched nanobowl structure could be further revealed by TEM characterization on a typical sample S@Z20-Z5 (Fig. 3). Figure 3a shows the bright-field TEM image of two single S@Z20-Z5 nanowire-branched nanobowls, clearly displaying the grafting of ZnO NWs on the surface of SnO2 nanobowls, which is consistent with the SEM results. A highly magnified TEM image (Fig. 3b) indicates the complete morphology and smooth surface of a randomly selected single ZnO NW with a diameter of ~25 nm. The high-resolution TEM (HRTEM) image (Fig. 3c) and the selected-area electron diffraction (SAED) pattern (Fig. 3d) of the randomly selected single ZnO NW on sample S@Z20-Z5 reveal that the branched ZnO nanowires have a single-crystalline structure. The lattice fringes of 0.248 nm and 0.281 nm in the single ZnO NW could be clearly identified, which correspond to the d-spacing values of the (101) and (100) planes of the hexagonal wurtzite ZnO phase (PDF#36–1451), respectively.

As shown in Fig. 4a, the crystal structures of hierarchical highly ordered SnO2 nanobowl branched ZnO NWs were investigated by XRD. Regarding pristine SnO2 nanobowls, after annealing at 550 °C in air, the measured diffraction peaks could be well indexed into a cassiterite SnO2 phase (PDF#41–1445). Specifically, the S@Z0 sample showed four characteristic diffraction peaks at 26.6°, 33.9°, 37.9°, and 51.8°, which correspond to the (110), (101), (200), and (211) planes of the cassiterite structure of SnO2, respectively. Compared to the pristine SnO2 nanobowls, the S@Z20 core-shell nanobowls obtained after the ALD-ZnO reaction displayed a new strong characteristic diffraction peak at 56.6°, which belongs to the zincite ZnO phase (PDF#36–1451). In addition, three weak diffraction peaks belonging to the SnO2 phase were not detected in the S@Z20 sample, which may be affected by the coating of the 20-nm ZnO film. Subsequently, ZnO NWs were further grown onto the surface of S@Z20 via a hydrothermal process (i.e., S@Z20-Z5), and three additional peaks at 31.7°, 34.4°, and 36.2° were detected, further confirming the hexagonal wurtzite structure of ZnO. Moreover, the prominent ZnO (002) peak indicated that the branched ZnO NWs had a preferential growth orientation along the c-axis. It should be noted that no other impurity peak was found in the XRD patterns, which confirmed the phase purity of the prepared samples.

Figure 4b-d and Figure S3 display the XPS spectra of pristine highly ordered SnO2 nanobowls (i.e., S@Z0) and sample S@Z20-Z5. The full spectrum of S@Z0 in Fig. S3a simply shows the peak positions of Sn 3d and O 1 s, revealing the exact SnO2 composition. By contrast, as shown in Fig. S3c, the additional peaks of Zn 2p and Zn LMM in the full spectrum of S@Z20-Z5 confirm the presence of ZnO in such a heterostructured sample. Specifically, the detailed XPS spectrum of Sn 3d in S@Z0 (Fig. 4b) displays two distinct peaks at binding energies of 487.0 and 495.3 eV, corresponding to the Sn 3d5/2 and Sn 3d3/2 core levels, respectively. For the detailed XPS spectrum of Sn 3d in S@Z20-Z5 (Fig. 4c), the asymmetric peak could be coherently fitted by two nearly Gaussian components, centered at 495.1 and 498.3 eV. The peak located at 487.0 eV could be assigned to the characteristic Sn 3d5/2 peak, which is identical to the typical value of SnO2. However, the other peak at a higher binding energy of 498.3 eV could be attributed to the Auger electron peak of Zn LMM, demonstrating the existence of Zn in the sample. Moreover, the Zn 2p XPS spectrum (Fig. 4d) of sample S@Z20-Z5 exhibits the characteristic Zn 2p3/2 and Zn 2p1/2 peaks centered at 1021.3 and 1044.3 eV, respectively, which confirms the presence of ZnO composition. The detailed O 1 s spectra of S@Z0 and S@Z20-Z5 can be found in Fig. S3b and d. Both asymmetric O 1 s peaks could be deconvoluted into two parts, assigned to oxygen in the SnO2 or ZnO crystal lattice and the surficial adsorbed oxygen, respectively.

The prepared samples were all synthesized in situ on MEMS structures to form the proposed gas sensors, as shown in Fig. 1. The JF02F gas sensing measurement system was used to evaluate the gas sensing properties of all the sensors. Typically, three representative MEMS-based sensors (i.e., sample S@Z0, S@Z20, and S@Z20-Z5) were chosen as examples for further investigation of gas sensing performance. The S@Z0 sample was only a highly ordered SnO2 nanobowl monolayer film with neither ZnO seed layers nor a hierarchical branched nanowire structure. The S@Z20 sample had a 20-nm-thick seed layer of ZnO film, and the S@Z20-Z5 sample had further branched ZnO NWs with optimal length and diameter on the basis of a ZnO seed layer. First, the response of a gas sensor is greatly
affected by the operating temperature. Hence, the relationship between the gas sensing response and the operating temperature was first investigated in Fig. 5a. For all the sensors, their gas sensing responses continued to grow as the operating temperature increased from 100 to 250 °C. All the sensors yielded maximum responses at 250 °C, indicating that the optimal operating temperature for the designed materials in this work could be chosen as 250 °C. However, all the responses began to decrease as the operating temperature further increased above 250 °C (i.e., 300 °C). H2S molecules will have difficulty reacting with adsorbed oxygen at a low operating temperature but will desorb before the reaction can occur at an excessively high operating temperature18. In addition, the diffusion rate of H2S molecules adsorbed on the material surface will improve with increasing temperature30. Therefore, at the optimal operating temperature of 250 °C, the gas sensing responses achieved maxima. The S@Z20-Z5 sensor displayed the highest response at any temperature.

Figure 5b shows the corresponding dynamic gas sensing response curves of all the samples (i.e., sample S@Z0, S@Z20, and S@Z20-Z5) with different hierarchical structures at the optimal operating temperature of 250 °C, obtained for the reducing gas of H2S with various concentrations ranging from 3 to 1 ppm. Apparently, the responses of all samples decrease as the H2S concentration decreases. More importantly, compared with the pristine highly ordered SnO2 nanobowl gas sensor (i.e., S@Z0), the designed hierarchical nanobowl SnO2@ZnO NW gas sensor (i.e., S@Z20-Z5) does exhibit superior gas sensing performance, which may be closely related to both the construction of the heterostructure and the effective increase in the specific surface area. Specifically, when the H2S concentration was fixed to 1 ppm, the response of S@Z20-Z5 was approximately 6.24, whose rate of resistance change (~5.24) was 2.6- and 1.6-fold those of the S@Z0 (~2.03) and S@Z20 (~3.34) sensors, respectively. Table 1 presents the sensing performance comparison of the prepared S@Z20-Z5 sensor with various other SnO2-based gas sensors fabricated on MEMS31–36. Comprehensively considering the related factors, including operating temperature, response values
and response/recovery time, the S@Z20-Z5 sensor shows improved performance among the MEMS-type SnO$_2$-based gas sensors.

To investigate the time dependence of the response, Fig. 5e shows the transient responses of all three samples exposed to 1 ppm H$_2$S at 250 °C. The response time and recovery time were measured as the time taken for the sensor output to change from 10 to 90% of the highest response variation. The recovery time of S@Z20-Z5 is 39 s, which obviously exhibits a better recovery property than the pristine S@Z0 sensor (i.e., 64 s). However, the recovery time of S@Z20-Z5 (i.e., 14 s) is slightly shorter than that of S@Z0 (i.e., 15 s). This indicates that compared with the pristine S@Z0 sensor, the S@Z20-Z5 sensor exhibits a faster response when exposed to H$_2$S gas. At the same time, the S@Z20-Z5 sensor possesses a better recovery property when turning off the gas and flushing with air. Actually, the existence of the SnO$_2$/ZnO heterojunction will improve the hole-electron separation rate at the interface, therefore improving the response and recovery speed to some extent.$^{37}$

In practice, good selectivity is a critical factor for a gas sensor, especially for distinguishing the given target gas from a complex atmosphere. Herein, the selectivity of the S@Z20-Z5 sensor was studied towards H$_2$S and various other reducing gases (1 ppm), such as ammonia (NH$_3$), acetone (CH$_3$COCH$_3$), methylbenzene (C$_7$H$_8$), and formaldehyde (HCHO), at an operating temperature of 250 °C, which is shown in Fig. 5c and Fig. S4. It can be observed apparently that the responses of all three samples to H$_2$S are significantly higher than those of other reducing gases, especially for the S@Z20-Z5 sensor, confirming the excellent selectivity. Generally, the selectivity is related to various complicated factors. First, H$_2$S has a relatively small band dissociation energy of 381 kJ/mol compared with other gases, which promotes decomposition and surface reactions during chemical adsorption at lower temperature.$^{38}$ As for the accurate calculation of the corresponding surface reaction kinetics, first-principles calculations based on density functional theory could be applied, which needs to be further investigated.$^{39}$ Second, the XPS characterization of the
SnO2@ZnO heterostructures before and after the H2S-sensing test conducted by Fu et al. has demonstrated that ZnO will react with H2S and transfer to ZnS, leading to a larger response since the conductivity of ZnS is higher than that of ZnO. Furthermore, the reaction between ZnO and adsorbed H2S is an exothermic and spontaneous process, while the reactions between ZnO and other test gases are endothermic and nonspontaneous. Therefore, the introduction of branched ZnO NWs further enhances the selectivity to H2S. Finally, H2S is considered to possess a larger adsorption capacity on the same surface adsorption area, which is attributed to the relatively small molecular size of H2S among these gas molecules. In addition, the S@Z20-Z5 sensor has a better selectivity than the one based on pristine SnO2 nanobowls. This phenomenon further confirmed the important role of the proposed branched ZnO NWs in improving the selectivity.

On the other hand, stability is also a key parameter from the viewpoint of practical gas sensing applications. The assessment of long-term stability was carried out on S@Z20-Z5 in ambient air for a month, as shown in Fig. 5d. Obviously, after a month, the S@Z20-Z5 sensor exhibited less than 5% variation in response when exposed to 5 ppm H2S, illustrating good long-term stability. However, it is undeniable that the response of the S@Z20-Z5 sensor exhibited a slight increase after a series of H2S gas sensing measurements for a month. The slightly higher response after a month may be caused by a few ZnS residual on the surface of the sensing material, which was transformed from ZnO in the presence of H2S and had a higher conductivity than ZnO. Fortunately, since the residual ZnS could be retransformed into ZnO more thoroughly at a higher temperature than the operating temperature of 250 °C, the response after a long-term test can return to the original value with the help of a high-temperature thermal treatment. Moreover, the top-view SEM image of a randomly selected area of S@Z20-Z5 after the above long-term tests is shown in Fig. S5. The intact hierarchical nanowire-branched nanobowl structure further demonstrated good long-term stability.

In general, the gas sensing mechanism is based on the surface adsorption/desorption model of oxygen species. It was observed in Fig. S6 that the resistances of all three sensors show a sudden decrease when introducing the reducing gas of H2S, indicating that the sensors exhibit typical n-type conductivity behaviors according to the acknowledged mechanism for the SMO-based resistance-type gas sensors. Specifically, when the n-type sensor was exposed to air, the physically adsorbed oxygen on the surface would capture electrons from the conduction band of sensing materials and turn into chemisorbed oxygen such as O2−, O22−, O− or O2−. Therefore, an
electron-depleted region formed underneath the material surface, causing the sensing material to be in a high-resistance state. Once the $n$-type sensor was exposed to the reducing gas of $\text{H}_2\text{S}$, the chemisorbed oxygen species on the surface would react with $\text{H}_2\text{S}$ and release the electrons back to the material, as typically shown in Eq. (1):

$$\text{H}_2\text{S} + 3\text{O}_2^{\text{ads}} \rightarrow \text{SO}_2 + \text{H}_2\text{O} + 6\text{e}^-$$ \hspace{1cm} (1)

Therefore, the resistance of the $n$-type sensor will achieve a rapid decrease when introducing the reducing gas, which is in accordance with the experimental results shown in Fig. S6. The three-dimensional schematic of $\text{S@Z20-Z5}$ exposed to $\text{H}_2\text{S}$ gas is shown in Fig. 6a.

The experimental results in Fig. 5b observably show that the sensing properties of the highly ordered $\text{SnO}_2$ nanobowl branched $\text{ZnO}$ NW sensor (i.e., $\text{S@Z20-Z5}$) were much better than that of the pristine $\text{SnO}_2$ nanobowl sensor (i.e., $\text{S@Z0}$). There are three main factors that satisfactorily account for the enhancement of gas sensing performance. First, due to the introduction of hierarchical branched $\text{ZnO}$ NWs, the increase in specific surface area effectively increases the active adsorption sites and enhances the sensing response. To provide direct experimental evidence for the increase in specific surface area, the electrochemically active surface areas of $\text{S@Z20}$ and $\text{S@Z20-Z5}$ were measured through electrical double-layer capacitance (EDLC) measurements in $\text{Na}_2\text{SO}_4$ solution on the basis that the double-layer capacitance ($C_{\text{dl}}$) is proportional to the electrochemically active surface area. The cyclic voltammetry (CVs) were tracked in the range of $-0.30$ to $-0.19$ V, where the current response should only refer to the charging of the double layer. The CV curves of the $\text{S@Z20}$ and $\text{S@Z20-Z5}$ electrodes at different scan rates (1, 2.5, 5, 7.5, 10, 15, 20, 25, and 30 mV/s) are shown in Fig. S7a, b, respectively. As a result, the capacitance of the $\text{S@Z20-Z5}$ electrode (0.223 mF/cm$^2$, Fig. S7d) is higher than that of the $\text{S@Z20}$ electrode (0.119 mF/cm$^2$, Fig. S7c), indicating the higher active surface area of the $\text{S@Z20-Z5}$ electrode, which is consistent with the SEM results. Therefore, on the basis of the CV measurements, the hierarchical heterostructured $\text{S@Z20-Z5}$ sample had a higher specific surface area than $\text{S@Z20}$, which effectively increased the number of gas adsorption sites.

Second, the cause of the resistance modulation could be the formation of the $\text{SnO}_2@\text{ZnO}$ heterojunction and $\text{ZnO}@\text{ZnO}$ homojunction at the corresponding interfaces. The separate band alignment diagrams of $\text{SnO}_2$ and $\text{ZnO}$ are displayed in Fig. 6b. Since the work function of $\text{ZnO}$ (5.2 eV) is larger than $\text{SnO}_2$ (4.9 eV), when the $\text{ZnO}$ film as well as $\text{ZnO}$ NWs were grown onto highly ordered $\text{SnO}_2$ nanobowls, the electrons would be

| Materials | Operating temperature [$^\circ$C] | Target gas | Response $R_a$/Rg | Response time [s] | Recovery time [s] |
|-----------|---------------------------------|------------|-------------------|-------------------|-------------------|
| Porous $\text{SnO}_2$ 3D architectures$^{31}$ | 240 | HCHO (0.5 ppm) | 2.9 | / | / |
| $\text{SnO}_2@\text{ZnO}$ composite nanofibers$^{32}$ | 250 | NO$_2$ (50 ppm) | 3.3 | 294 | / |
| $\text{SnO}_2@\text{ZnO}$ nanowires (100 ppm) | 200 | CH$_3$OH (15 ppm) | 3.0 | / | 264 |
| Hierarchical $\text{SnO}_2@\text{ZnO}$ NWs$^{33}$ | 110 | CH$_3$CH$_2$OH (1 ppm) | 18 | 25 | 18 |
| $\text{SnO}_2$/$\text{ZnO}$ core-shell nanosheets$^{34}$ | 250 | H$_2$S (1 ppm) | 3.4 | 14 | 93 |
| Hierarchical nanobowl $\text{SnO}_2@\text{ZnO}$ NWs (this work) | 250 | CH$_3$OH (2 ppm) | 4.29 | / | / |
| Porous $\text{SnO}_2@\text{ZnO}$ hybrid nanotubes$^{35}$ | 250 | H$_2$S (1 ppm) | 0.223 | / | 6.24 |

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transferred from SnO₂ to ZnO to equalize the Fermi level, leading to the formation of a potential barrier at the n-n heterojunction interface (Fig. 6c)⁴⁸. As a result, the resistance of the n-type S@ZnO NW sensor (Rₐ) achieved a further increase in air because of the additional existence of a potential barrier formed at the SnO₂@ZnO heterojunction interface. Correspondingly, when the S@ZnO NW sensor was exposed to the reducing gas of H₂S, the decrease of the heterojunction barrier could help further reduce the resistance (Rₐ), leading to the enhancement of the sensing response defined as Rₐ/Rₕ. Since the conductivity of the reaction product ZnS is higher than that of ZnO, the resistance of the whole material would achieve a further decrease after introducing H₂S and undergoing such a transformation reaction⁴⁰. Correspondingly, when the material was exposed to air again, the small amount of ZnS on the surface reacted with adsorbed oxygen and retransformed into ZnO at the high operating temperature⁴². Therefore, the introduction of ZnO film and branched ZnO NWs further improves the sensitivity of the heterostructured SnO₂@ZnO sensors. Meanwhile, as mentioned above, the spontaneous reaction between ZnO and H₂S enhances the selectivity of the heterostructured sensors for H₂S detection as well.

ZnO is exposed to H₂S, a small amount of ZnO reacts with the adsorbed H₂S and turns into ZnS on the surface, as shown in Eq. (2):⁴⁹

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}
\]  

(2)

Since the conductivity of the reaction product ZnS is higher than that of ZnO, the resistance of the whole material would achieve a further decrease after introducing H₂S and undergoing such a transformation reaction⁴⁰. Correspondingly, when the material was exposed to air again, the small amount of ZnS on the surface reacted with adsorbed oxygen and retransformed into ZnO at the high operating temperature⁴². Therefore, the introduction of ZnO film and branched ZnO NWs further improves the sensitivity of the heterostructured SnO₂@ZnO sensors. Meanwhile, as mentioned above, the spontaneous reaction between ZnO and H₂S enhances the selectivity of the heterostructured sensors for H₂S detection as well.

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**Fig. 6 Schematics of the reducing gas sensing mechanism in the hierarchical highly ordered nanobowl SnO₂@ZnO NWs.** 

- **a** The three-dimensional schematic of the hierarchical highly ordered nanobowl SnO₂@ZnO NWs exposed in H₂S gas; 
- **b**, **c** the schematic energy band diagrams for the hierarchical SnO₂@ZnO NWs: **b** in separate state and **c** in air. The band structure data in figure (b) were determined from the literature⁴⁸.
**Materials and methods**

**Chemicals and reagents**

Analytical grade tin (IV) chloride hydrate (SnCl₄) was obtained from Alfa Aesar. Zinc nitrate hexahydrate [Zn(NO₃)₂ · 6H₂O] and hexamethylenetetramine (C₆H₁₂N₄) were purchased from Aladdin. Sodium dodeyl sulfate (SDS) as the surfactant was obtained from Sinopharm Chemical Reagent Co., Ltd. The precursor materials used for depositing the ZnO layer were diethyl zinc [(C₂H₅)₂Zn, DEZ, Sigma Aldrich, 99.999%] and deionized (DI) water. All chemicals were used as received without any further purification. Other chemical reagents employed in our experiments were analytical grade, and the gases were ultrahigh pure (99.999%). All aqueous solutions were prepared with DI water acquired from a Millipore Q purification system (resistivity >18 MΩ·cm).

**Synthesis of highly ordered SnO₂ nanobowls**

The highly ordered SnO₂ nanobowls were synthesized via a modified hard template method reported before. The suspension of monodispersed PS spheres 800 nm (2.5 wt% in DI water) in diameter was synthesized according to our previous work. Then, the PS suspension was diluted in ethanol of the same volume and subjected to ultrasonic treatment for absolute uniformity. The precursor solution was 0.1 M aqueous SnCl₄ (100 mL). The ethanol-diluted PS suspension was slowly injected into the precursor solution, and the monolayer PS spheres could float on the surface of the precursor solution and began to self-assemble at the air/solution interface. Specifically, the control of the injection rate was conducted by adjusting the inclination angle of the well-cleaned and oxygen plasma pretreated glass slide, which was applied as a drainage plate. Subsequently, the floating PS monolayer was transferred to the MEMS substrate by a simple picking-up process and thoroughly dried at room temperature. Due to the capillary effect, the PS monolayer was applied as a drainage plate. Subsequently, the ultrasonic simple picking-up process and thoroughly dried at room temperature. The PS monolayer was transferred to the MEMS substrate by a simple picking-up process and thoroughly dried at room temperature.

**Synthesis of highly ordered nanobowl SnO₂@ZnO films**

ZnO seed layers of different thicknesses, namely, 50, 100, and 150 cycles, were deposited at 200 °C on as-prepared highly ordered SnO₂ nanobowls in a BENEQ TFS-200 ALD system. Briefly, DEZ and DI water were used as the zinc (Zn) and oxidant sources, respectively. The highly ordered SnO₂ nanobowls were alternately exposed to the vapor pulse of the DEZ and DI water precursors in the ALD reactor chamber using high purity argon gas as the carrier gas. Meanwhile, the high purity Ar as the purge gas purged the gaseous byproducts and residual gas out of the chamber between two valid pulses, effectively avoiding unexpected gas reactions. For all samples, the deposition process in each growth cycle briefly includes a 0.2 s pulse of DEZ, a 10 s purge, a 0.2 s pulse of DI water and a 10 s purge. The different desired thicknesses of ZnO seed layers can be achieved by repeating different specific ALD growth cycles.

**Synthesis of hierarchical highly ordered nanobowl SnO₂@ZnO NWs**

ZnO NWs were grown on highly ordered nanobowl SnO₂@ZnO films with different ZnO seed layers through a traditional hydrothermal process. In particular, an aqueous solution containing 25 mM Zn(NO₃)₂ · 6H₂O and 25 mM C₆H₁₂N₄ was prepared as the precursors for ZnO NW growth and transferred into 80 mL Teflon-lined stainless steel autoclaves. Then, highly ordered nanobowl SnO₂@ZnO films on MEMS substrates were submerged in the solution with face down. The hydrothermal reactions were carried out at 80 °C for different reaction times, namely, 1, 3, 5, and 8 h, and then cooled to room temperature. The substrates were then removed from the solution, rinsed thoroughly with DI water and dried with high pure nitrogen.

**Instruments and characterization**

A BENEQ TFS-200 ALD system was used to deposit the ZnO seed layers. The thicknesses of the ZnO films deposited on flat silicon substrates were measured by a SOPRA GES-5E spectroscopic ellipsometry (SE) system. The morphologies of all the samples were recorded on a Zeiss SIGMA HD field-emission SEM and an FEI Tecnai G₂ F20 S-TWIN field-emission TEM. Wide-angle XRD patterns were collected on a Bruker D8 Advance powder X-ray diffractometer with Ni-filtered Cu-Kα₁ radiation (40 kV, 40 mA, 1.5406 Å). XPS measurements were conducted on a PHI 5000 VersaProbe system using an Mg-Kα X-ray source.

**Gas sensing performance measurements**

For the gas sensing measurements, hierarchical highly ordered nanobowl SnO₂@ZnO NWs were prepared in situ on MEMS heating appliances. Then, the ultrasonic wire bonding technique was applied to connect the fabricated MEMS device with the external circuit. A JF02F gas sensing measurement system was used to characterize the sensing characteristics of the fabricated hierarchical highly ordered nanobowl SnO₂@ZnO NW sensors for reducing gases, namely, H₂S, NH₃, CH₃COCH₃, C₆H₁₀, and HCHO. In this work, for n-type SMO materials, the gas sensing response (R) in the reducing-gas measurements was defined as R = Ra/Rg, where Ra represents the resistance of materials in air and Rg represents the
displayed a high sensitivity (Ra/Rg) of 6.24, a fast response time, and excellent selectivity when detecting 1 ppm H2S at 250 °C, whose rate of resistance change (i.e., 5.24) is 2.6 times higher than that of the pristine SnO2 nanobowl sensor. The substantially improved sensing performance could be mainly attributed to the synergistic effect of the hierarchical heterostructures, including increased specific surface area, the formation of heterojunctions and homojunctions, as well as the additional reaction between ZnO and H2S. Based on our results, such well-designed hierarchical highly ordered nanobowl SnO2@ZnO NW gas sensors are good candidates for enhanced sensitive and selective H2S detection with long-term stability and repeatability.

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Author contributions
LYZ, KPY, and HLL conceived and designed the project. LYZ and KPY performed the experiments. LYZ, KPY, JHY, CZH, HPM, XMJ, AD, HLL, and DWZ analyzed the data. LYZ, KPY, and HLL wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflict of interest
The authors declare that they have no conflict of interest.

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Conclusions
In conclusion, hierarchical highly ordered SnO2 nanobowl branched ZnO NWs were synthesized through a sequential process combining hard template processing, atomic-layer deposition and hydrothermal processing. The designed hierarchical sensing materials were prepared in situ on MEMS, which is expected to achieve long-term stability and low power consumption. Specifically, the hierarchical nanobowl SnO2@ZnO NW sensor displayed a high sensitivity (Ra/Rg) of 6.24, a fast response and recovery speed (i.e., 14 s and 39 s, respectively), and an excellent selectivity when detecting 1 ppm H2S at 250 °C, whose rate of resistance change (i.e., 5.24) is 2.6 times higher than that of the pristine SnO2 nanobowl sensor. The substantially improved sensing performance could be mainly attributed to the synergistic effect of the hierarchical heterostructures, including increased specific surface area, the formation of heterojunctions and homojunctions, as well as the additional reaction between ZnO and H2S. Based on our results, such well-designed hierarchical highly ordered nanobowl SnO2@ZnO NW gas sensors are good candidates for enhanced sensitive and selective H2S detection with long-term stability and repeatability.

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