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Gas Sensing of SnO₂ Nanocrystals Revisited: Developing Ultra-Sensitive Sensors for Detecting the H₂S Leakage of Biogas

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As a typical mode of energy from waste, biogas technology is of great interest to researchers. To detect the trace H₂S released from biogas, we herein demonstrate a high-performance sensor based on highly H₂S-sensitive SnO₂ nanocrystals, which have been selectively prepared by solvothermal methods using benzimidazole as a mineralization agent. The sensitivity of as-obtained SnO₂ sensor towards 5 ppm H₂S can reach up to 357. Such a technique based on SnO₂ nanocrystals opens up a promising avenue for future practical applications in real-time monitoring a trace of H₂S from the leakage of biogas.

Nowadays, energy and environmental problems have become two of the greatest challenges, which strongly influence the social manner and quality of people all over the world^{1–3}. As a renewable energy source, biogas technology, which converts wastes into energy, has attracted great attention in many countries, and been well developed. Biogas mainly contains methane (CH₄), together with a trace of other toxic gases, in which H₂S is identified as the main toxic component⁴. Due to the high toxicity of H₂S, it is extremely detrimental for human being to be exposed to H₂S if the leaking of biogas happens. At present, 4 ppm is the maximum value of H₂S, allowed by the fuel gas specifications for pipeline transportation. Although there are physical and chemical absorption as well as biological treatments of H₂S for biogas purification, it is still difficult to completely remove H₂S gas from biogas with low-cost methods^{5,6}. To prevent potential risks of biogas leakage, it is necessary to realize real-time monitoring a trace amount of H₂S gas (<5 ppm) released from biogas during production and transportation processes.

Gas sensors are of great interest due to their capability for a real-time analysis of gaseous chemicals in a wide range of applications^{7–17}. Accordingly, different gas sensors have been readily applied in the biogas process^{18,19}. However, there is no report on detecting H₂S from biogas during its production and transportation processes. To detect a trace amount of H₂S gas, it is a prerequisite that high-performance sensing material towards H₂S gas should be available. It is well recognized that the sensing material is the core of gas sensors. Typically, tin oxide (SnO₂) is a well-known gas-sensing material, which has been intensively studied with various shapes and morphologies for its detection towards various gases^{20–31}. Meanwhile, numerous efforts have been exerted on the synthesis strategies of favorable SnO₂ structures to detect H₂S gas^{32–40}. Especially, Lee and his co-workers developed a synthetic route to obtain the CuO-functionalized SnO₂ nanowires with a response as high as 419 towards 20 ppm H₂S³⁵. Unfortunately, the sensor requires a temperature as high as 400°C to achieve a satisfied function. Therefore, it is necessary to develop highly H₂S sensitive sensors based on novel materials with higher selectivity, lower-detection limit, and low-power consumption for monitoring the H₂S gas from the leakage of biogas.

Herein, we report a solvothermal method for the preparation of high-performance SnO₂ nanocrystals with benzimidazole as a mineralization agent. The sensor with SnO₂ nanocrystals as the sensing material shows an ultrahigh sensitivity towards trace H₂S gas, and a high selectivity to H₂S in CH₄. Moreover, structural characterizations and sensing mechanism analysis were undertaken to study the correlation between the sensor performance and the materials structure. It is expected that these as-prepared SnO₂ nanocrystals are promising for a real-time monitoring of trace H₂S during biogas production and transportation processes.

Figure 1 | XRD patterns of the SNC1, SNC2 and SNC3.

Results

In this work, different shapes and morphologies of SnO_2 nanocrystals could be easily obtained under solvothermal conditions with benzimidazole as a mineralization agent. The amount of benzimidazole plays crucial roles in determining the growth of SnO_2 nanocrystals. When the amount of benzimidazole is 0.1, 0.3 and 0.6 g respectively, while other conditions kept the same, different SnO_2 samples can be prepared accordingly SnO_2 nanocrystals, denoted as SNC1; longer SnO_2 nanocrystals, denoted as SNC2; SnO_2 larger nanocrystals, denoted as SNC3. The phase of as-prepared SnO_2 nanocrystals (SNC1, SNC2 and SNC3) was confirmed as pure tetragonal phase of SnO_2 (JCPDS Card 41-1445) by X-ray diffraction (XRD) measurements, as shown in Figure 1.

Transmission electron microscopy (TEM) was employed to further examine the representative morphologies and structures of as-prepared SnO_2 nanocrystals. TEM image in Figure 2a shows that SNC1 exists as homogeneous nanocrystals. In the high-resolution

Figure 2 | TEM images of (a and b) SNC1, (c and d) SNC2 and (e and f) SNC3.

Figure 3 | The size statistics of SNC1, SNC2 and SNC3.

TEM (HR-TEM) image (Figure 2b), it clearly shows that the size of SNC1 nanocrystals is about 3.4 ± 0.8 nm. The SNC2 has an average edge length of 7.4 ± 0.5 nm and width of 4.8 nm as shown in Figure 2d. Meanwhile, the SNC3 sample shows an average diameter of 5.2 ± 0.8 nm (Figure 2e and f). TEM gives us a direct proof that the present method is very effective for controlling the size and morphology of SnO_2 nanocrystals. To support our given data, the size distribution for three SnO_2 samples is also given in Figure 3. Similarly, the dynamic light scattering (DLS) characterization gave larger diameters (Figure S1) compared to the one from TEM images, which is probably due to the existence of hydrated layers around the particle surfaces and the aggregation of SnO_2 nanocrystals as well. Moreover, we also found that only homogeneous SnO_2 samples were obtained without the use of benzimidazole. No obvious difference has been observed when the ratios of water and ethanol were changed (Figure S4 and S5). Electron energy loss spectroscopy (EELS) was further used to characterize SNC1 (Figure S2). No other elements (C, N) originated from benzimidazole were detected on SNC1, which further proved the high purity of our samples. Here, the roles of benzimidazole should be included: directing the growth of inorganic

Figure 5 | (a) Sensors responses to CO, H₂, NH₃, SO₂, CH₄, and H₂S at 125°C and Sensors responses of SNC1 to various gases with different operating temperatures (the inset of Figure 5).

nanocrystals⁴¹; aggregation effect or assembly due to its rich interactions (hydrogen bond, π - π stacking, and van der Waals interaction)⁴². Under these interactions, different shapes and morphologies of SnO_2 nanocrystals could be obtained by adjusting the amount of benzimidazole used.

Nitrogen isotherm adsorption-desorption curves together with the pore size distributions of these as-synthesized SnO_2 nanocrystals are given in Figure 4. In Figure 4a, SNC1 shows a typical type-IV isotherm with H2-type hysteresis loop⁴³. Base on the Barrett-Joyner-Halenda (BJH) equation, the main pore size (Figure 4b) for SNC1 is determined as 3.8 nm, which further confirms a uniform pore size distribution. The BET specific surface area (S_{BET}) for SNC1 is $223.6 \text{ m}^2 \cdot \text{g}^{-1}$. The higher S_{BET} of the adsorption-desorption curve shows that SNC1 has the larger inter particle distance and homogenized sizes. SNC2 and SNC3 exhibit a type IV isotherm with H2-type hysteresis loops as shown in Figure 4a. The high S_{BET} of SNC2 ($181.2 \text{ m}^2 \cdot \text{g}^{-1}$) shows the large interparticle distances as revealed in Figure 2d. The smaller hysteresis loop and the S_{BET} of SNC3 ($109.7 \text{ m}^2 \cdot \text{g}^{-1}$) is probably a result of the severe aggregation in the sample. These results further indicate that it is effective to tailor the aggregated structure of SnO_2 nanocrystals with a high S_{BET} by simply changing the amount of benzimidazole.

High S_{BET} metal oxides have been demonstrated to be promising for gas sensing. Especially, a sensitive gas sensor with high selectivity for trace H₂S is extremely important to detect the biogas. In this study, a comparison of the sensor response of SnO_2 nanocrystals to 25 ppm of various gases at operating temperature of 125°C is shown in Figure 5 and S8. Notably, all the sensor response towards different gases are all less than 2 orders of magnitude as compared to the signal from H₂S. From the plot, it is clear that SNC1 shows not

Figure 4 | (a) N₂ isotherm adsorption-desorption curves and (b) the pore-size distribution of SNC1, SNC2 and SNC3.

Figure 6 | Response and recovery characteristics of SNC1 sensors upon to 5 ppm H₂S at 45, 125, 160 and 275 °C, respectively.

only enhanced sensitivity towards H₂S but also a very high selectivity. The variation of sensitivity of SNC1 under different operating temperature towards 25 ppm of H₂S is shown in the Table (the inset of Figure 5). It is clear that SNC1 has an obvious response to H₂S gas between 45 °C and 200 °C, and excellent selectivity towards H₂S gas. The excellent selectivity of SNC1 facilitates the application for detecting H₂S.

Figure 6 shows the response and recovery of SNC1 sensors upon exposure to 5 ppm H₂S at 45, 125, 160 and 275 °C, respectively. It is obvious that the sensor shows switch-like characteristics after an H₂S exposure, and the response intensity is extremely high. At operating temperatures of 45 °C and 125 °C, the response times are about 120 and 224 s, respectively, while the recovery time is both several hours. Raising the operating temperature can immediately shorten both the recovery and response time. At 160 °C, the response of the sensor is the most sensitive one ($S = 320$). Detecting H₂S with a trace level (<5 ppm) at such a low temperature is very useful for real-time monitoring H₂S gas released from biogas during production and

transportation processes. The results are also excellent in comparison with previous results for tin oxide or modified tin oxide as gas sensor for H₂S detection, as shown in Table 1.

The typical response-recovery curves of the sensors made from the as-synthesized SNC1 and commercial SnO₂ (c-SnO₂) exposed to different concentrations of H₂S ranging from 0.5 ppm to 30 ppm were shown in Figure 7a. Figure 7b displays the sensor response of different SnO₂ nanocrystals towards various concentrations of H₂S. The SNC1 sensor shows a much larger response magnitude to each concentration of H₂S, compared with other SnO₂ sensors. It is obvious that the sensor based on SNC1 is able to detect a wide range of H₂S concentrations, with detection limit in the ppb level while the response towards 0.5 ppm of H₂S is still as high as 20.4, indicating its excellent sensitivity and stability. However, the response for SNC3, c-SnO₂ and SNCb (Figure S9) are extremely slow, probably due to their aggregated characteristics and lower S_{BET} (The characterization of c-SnO₂ is shown in Figure S6 and S7). When H₂S concentration is in range of 0.5–30 ppm, the logarithm of the sensor response shows a

Table 1 | Comparison of gas-sensing characteristics of SnO₂-based gas sensor

Materials	H ₂ S Concentration (ppm)	Response $S = R_a/R_g$	Work Temperature (°C)	Ref.
SnO ₂ nanofibers	4	23	300	28
SnO ₂ nanocrystals	20	27	150	32
SnO ₂ thin films	80	96	100	33
SnO ₂ submicrotubes	0.5	11.7	160	34
Ag-SnO ₂ nanopowders	50	55	332	35
CuO doped SnO ₂ nanowires	20	419	400	36
Fe/SnO ₂ composite	67.9	50	250	37

Figure 7 | (a) Response and recovery characteristics of SNC1 and c-SnO₂ sensors at different concentration of H₂S at 160°C. (b) The sensor responses of SnO₂ nanocrystals at different concentration of H₂S at 160°C.

good linearity against the logarithm of the gas concentrations as shown in Figure S10, which is in agreement with the theory of the power laws for semiconductor sensors³³.

Figure 8a shows the sensor response of SNC1 at different working temperatures to 5 ppm H₂S. The sensor response S increases and reaches its maximum at about 160°C and then decreases rapidly with the increase of temperatures. Figure 8b displays the sensor response of SNC1 at different working temperatures to 100 ppm CH₄. The sensor response S is similar from 45°C to 350°C, and reaches its maximum of 3.0 at about 200°C. Figure 8c and d show a continuous

measurement of 5 ppm H₂S and 100 ppm CH₄. The result indicates that the SNC1 sensor have good repeatability.

An alternate experiment is also carried out to detect the composite gases between biogas (5 ppm of H₂S gas and 95 ppm of CH₄) and 100 ppm pure CH₄ at 160°C (Figure 9). Firstly, a low signal was observed at 3.1 after exposed to 100 ppm of CH₄. Then, the response increased sharply to 335 after encountering a composite biogas with 5% H₂S. Similarly, we can also test the repeatability of our sensor performance by switching the working environment between pure CH₄ and a composite biogas. It is clear that no obvious deterioration

Figure 8 | (a) the response of SNC1 sensor to 5 ppm H₂S at different working temperature; (b) the response of SNC1 sensor to 100 ppm CH₄ at different working temperature; (c and d) the repeat of SNC1 sensor to detect H₂S and CH₄ at 160°C, respectively.

Figure 9 | A repeatedly alternate experiment to detect the composite gases between biogas (5 ppm of H_2S gas and 95 ppm of CH_4) and CH_4 at 160°C .

of the response can be observed during this experiments although there indeed exists a slightly drop after extended cycles. It can be concluded that SNC1 nanoparticles-based H_2S sensor is promising for biogas composition monitoring.

Discussion

The change in the electrical resistance of a semiconductor is closely related to the chemical properties of the surface oxygen. Oxygen is adsorbed on SnO_2 nanocrystal surface in different forms depending on the temperature, from physisorption (molecular form) to chemisorption (dissociative form) as temperature increase^{33,42}. These oxygen adsorbates (O_2^- , O^- and O^{2-}) on the surface of n-type SnO_2 induce an electron depletion layer, resulting in the decrease in carrier concentration and the increase in the surface potential barrier^{42–46}. Upon exposures to reducing gases like H_2S , the surface oxygen is consumed due to the chemical reaction.

Then the electrons donate back to the surface of semiconductor, leading to the decrease in electrical resistance. Therefore, the concentration of surface oxygen depends on the concentration of the reducing gas as the same operating temperature. The chemical adsorption of oxygen and its reaction with reducing gases under

lie the sensing mechanism of SnO_2 nanocrystals³². It can be expressed by Eq.(1),

$$S = \frac{R_a}{R_g} \propto P_{\text{H}_2\text{S}}^m \quad (1)$$

Where $P_{\text{H}_2\text{S}}$ is the concentration of H_2S gas in air, the power law exponent m takes the value of 1, 0.5 or 0.25 respectively depending on the species of chemisorbed (ionisorbed) oxygen (O_2^- , O^- and O^{2-} correspondingly) and thus on the temperature. Comparing the value of m obtained from experiment results ($m = 0.8$) with that from theoretical analysis, that is

$$0.5 < m < 1$$

This relation indicates that at 160°C , the oxygen chemical desorption on SnO_2 nanocrystals surfaces might be dominated by O_2^- and O^- simultaneously, which is in accordance to the TPD, FTIR and EPR studies conducted on SnO_2 surfaces^{47,48}, indicating that the molecular form (O_2^-) dominates below 150°C , and above this temperature the ionic species dominate, predominately as O^- below 400°C and O^{2-} above 400°C , which is then directly incorporated into the lattice above 600°C .

The proportions of O_2^- and O^- involved here can be calculated through the reaction Eqs.(2,3):

$$x + y = 1 \quad (3)$$

Where x and y are the proportions of O_2^- and O^- respectively. And we obtain:

$$S = \frac{R_a}{R_g} \propto P_{\text{H}_2\text{S}}^{1/1+y} \quad (4)$$

Inserting the value of m into Eq. (4) leads to: $x = 0.75$, $y = 0.25$. Therefore, oxygen might be ionisorbed on SnO_2 surfaces as O_2^- and O^- with the proportion ratio of 3:1 at 160°C , which needs to be demonstrated by further spectroscopy study. The above discussion suggests that the power law exponent is characteristic of the surface reaction. It determines the dominating species of oxygen adsorbates and the proportion.

The height of energy barrier to electron transport between neighboring grains in the SnO_2 is an important factor, which determines sensitivity of the material⁴⁷. The temperature dependence of the conductivity of a semiconductor can be approximated by the Arrhenius equation⁵⁰:

Figure 10 | Schematic illustration of chemical reactions on SnO_2 nanocrystals surface underlying H_2S sensor mechanism.

$$\sigma = \sigma_0 \exp\left(\frac{-eV_s}{kT}\right) \quad (5)$$

Where σ_0 is a factor that includes the bulk in granular conductance, k the Boltzmann's constant, T the absolute temperature, and eV_s the potential energy barrier at the interface between two neighboring particles.

$$eV_s = \frac{e^2 N_t^2}{2\epsilon_r \epsilon_0 N_d} \quad (6)$$

Where N_t is the surface density of adsorbed oxygen ions (O_2^- or O^-), $\epsilon_r \epsilon_0$ is the permittivity of the semiconductor, and N_d is the volumetric density of the electron donors. Clearly, the energy barrier is a function of temperature and atmosphere (oxygen partial pressure), each of these parameters influences the energy barrier, conductivity, and thus the sensitivity. Further, eV_s depends on the particle size, especially when the particle size is reduced to nanometer or in the order of the thickness of charge depletion layer (X_d). Different particle size corresponds to different ratio of X_d to the radius of the particles, provided that the absolute value of X_d is relatively independent of particle size^{49,51,52}. If the particle size is much larger than the X_d , the band bending or aggregated is restricted to the surface region of the particle, as shown in Figure 10. When the particle size is nanometer, the properties of particles change dramatically due to solid-gas interactions. SNC1 is anticipated that both S_{BET} and the size of particles can influence sensor response.

In summary, we have successfully obtained a high-performance SnO_2 sensor for detecting trace H_2S from the biogas. By means of a control over the size and morphology of SnO_2 nanocrystals, the sensor performance can be accordingly tuned due to the difference in the S_{BET} of the sensor materials. The mechanism of gas sensing towards H_2S has been discussed in detail. The sensor built on the as-prepared SNC1 shows promising sensing properties towards a real time monitoring of trace H_2S from the leakage of biogas.

Methods

Hydrothermal synthesis of SnO_2 nanocrystals. In a typical synthesis, 0.35 g of $SnCl_4 \cdot 5H_2O$ and 0.1 g of benzimidazole were first dissolved into mixed solution with 20 mL of distilled H_2O and 20 mL of ethanol, and then transferred into a 50 mL Teflon-lined stainless-steel autoclave at 180°C for 20 h. Finally, the obtained white sample was rinsed with deionized water and ethanol for several times, and dried in ambient conditions. In order to investigate the effect of benzimidazole on the morphology of final products, a series of controlled experiments were also conducted, and the amount of benzimidazole is 0.3 and 0.6 g, respectively.

Characterization. The morphology and structural characteristics were observed using X-ray diffraction (XRD, Rigaku D/max 2500 diffractometer), high-resolution transmission electron microscopy (HRTEM, JEOL 2010) equipped with an electron energy loss spectroscopy (EELS), and nitrogen adsorption-desorption isotherms (ASAP 2020 nitrogen adsorption apparatus). The Brunauer-Emmett-Teller (BET) specific surface areas (S_{BET}) were calculated using the BET equation. Desorption isotherm was used to determine the pore size distribution using the Barret-Joyner-Halender (BJH) method. Particle size range was estimated using a dynamic light scattering (DLS) device (Malvern Zetasizer Nano ZS90).

Sensor measurements. The fabrication and testing principles of the gas sensor are similar to that described in our previous reports. Firstly, the SnO_2 samples were mixed with terpineol to form a paste and then coated onto the outside surface of an alumina tube with a diameter of 1 mm and a length of 5 mm. A platinum coil through the tube was employed as a heater to control the operating temperature. To improve their stability and repeatability, the gas sensors were aged at 300°C for 10 days in air. Here, the sensing properties of the sensors were measured by a NS-4003 series gas-sensing measurement system (China Zhong-Ke Micro-nano IOT, Internet of Things, Ltd.). The relative humidity (RH) is about 45%. The response and recovery times were defined as the time required for a change of the resistance to reach 90% of the equilibrium value after injecting and that for removing the detected gas, respectively. When air and ppm-level target gas were flowed through the sensor element, the corresponding steady-state resistances of the sensor in air (R_{air}) and in the air-gas mixture (R_{gas}) were recorded, respectively. The sensor response (S) for oxidizing gas (NO or NO_2) is defined as the ratio of R_{gas}/R_{air} , while the response for reducing gas (H_2S , H_2 , CO or CH_4) is defined as the ratio of R_{air}/R_{gas} .

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Author contributions

J.M.M. proposed and designed the experiments. L.M. carried out the synthetic experiments and conducted the characterization. L.M. performed the HRTEM, SEM characterization and structural analysis. L.M. analyzed the data. Y.J.C. and L.M. prepared the gas sensors. L.M. and J.M.M. wrote the manuscript. All the authors participated in discussions of the research.

Additional information

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