Synthesis and Characterization of Highly Sensitive Hydrogen (H₂) Sensing Device Based on Ag Doped SnO₂ Nanospheres

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Abstract: In this paper, pure and Ag-doped SnO₂ nanospheres were synthesized by hydrothermal method and characterized via X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), and X-ray photoelectron spectra (XPS), respectively. The gas sensing performance of the pure, 1 at.%, 3 at.%, and 5 at.% Ag-doped SnO₂ sensing devices toward hydrogen (H₂) were systematically evaluated. The results indicated that compared with pure SnO₂ nanospheres, Ag-doped SnO₂ nanospheres could not only decrease the optimum working temperature but also significantly improve H₂ sensing such as higher gas response and faster response-recovery. Among all the samples, the 3 at.% Ag-doped SnO₂ showed the highest response 39 to 100 µL/L H₂ at 300 °C. Moreover, its gas sensing mechanism was discussed, and the results will provide reference and theoretical guidance for the development of high-performance SnO₂-based H₂ sensing devices.

Keywords: Ag doping; SnO₂ nanospheres; synthesis and characterization; H₂ sensing device

1. Introduction

Hydrogen (H₂), as one of the cleanest, most efficient, abundant and renewable energies, has attracted worldwide attention in the past few decades [1–4]. It has extensive applications in fuel cells, nuclear power plants, industry, petroleum refining and aerospace [5,6]. However, H₂ will be easy to explode in a wide range of concentration (4–75%) with low ignition energy (0.02 mJ) [7]. Therefore, in industrial process control and applications, it is necessary to develop rapid and accurate sensor to detect the leakage of hydrogen storage, transportation and usage [8,9].

Numerous types of H₂ sensors based on different principles like the resistive type, thermoelectric type and optical fiber have been reported [10–13]. Among these, metal-oxide semiconductor (MOS) sensors take a special position [14–16]. In particular, SnO₂ is particularly remarkable due to its high electron mobility, low cost and good chemical properties [17]. Metal doping is one of the most effective approaches to enhance the gas-sensing performances [18–20]. For example, Wang et al. studied Au-loaded SnO₂ gas sensor with several dopants concentrations, and showed that 4.0 at.% Au-loaded SnO₂ exhibited the highest response value 25 toward 100 ppm H₂ at 250 °C [17]. Dae-Hyun Baek et al. reported MoS₂ gas sensor functionalized by Pd successfully detected hydrogen gas diluted by air at room temperature [18]. Liu et al. reported 1 wt % Co-doped SnO₂ nanofibers, and the
measured results exhibited the highest response to 24 along with a short response and recovery time (2 s, 3 s) toward 100 ppm H$_2$ at 330 °C [21]. Mehar Bhatnagar et al. investigated the incorporation of C in SnO$_2$ nanoparticles, and excellent selectivity towards H$_2$ and ethanol in the low temperature range [22]. Some works have been reported that researchers use Ag as a catalytic dopant on the surface of SnO$_2$ to improve its performance of gas sensing. For example, Wu et al. reported that the Ag-doped SnO$_2$ sensor response was 2.24, and the response-recovery time were as short as 34 s and 68 s, respectively in an ethanol gas detection system [23]. Based on the density functional theory and the first-principles, Jin et al. built the pure and Ag-doped SnO$_2$ models and gas adsorption models, and interesting calculations were conducted [24]. However, the influence of the ratio of Ag dopant in SnO$_2$ on detecting H$_2$ has not been reported. We further focused on the morphology of SnO$_2$ nanostructures and the ratio of Ag dopant in SnO$_2$ for the purpose of H$_2$ detection.

In this work, we have successfully synthesized pure and Ag-doped SnO$_2$ nanospheres materials and systematically researched their gas sensing performances to H$_2$. The effects of Ag doping on SnO$_2$-based H$_2$ detection response were analyzed, which showed a significant dependence of H$_2$ sensing performance on Ag concentration. The results indicated that the introducing of moderate Ag plays an important role in improving the sensing performances of pure SnO$_2$ nanospheres to H$_2$, in terms of lower optimal working temperature, higher gas response and shorter response-recovery time. Moreover, its gas sensing mechanism was also discussed in detail.

2. Materials and Methods

2.1. Materials

All raw chemicals were analytical graded and purchased from Chongqing Chuandong Chemical Reagent Co., Ltd. and were used as received without any further purification.

2.2. Synthesis of the Sensing Materials

Undoped and Ag-doped SnO$_2$ nanosphere gas sensitive materials were prepared using the simple hydrothermal method. First, 2.67 g of sodium stannate (Na$_2$SnO$_3$·3H$_2$O), 2.4 g of sodium hydroxide (NaOH) and 0.8 g of citric acid (C$_6$H$_8$O$_7$·H$_2$O) were dissolved into the binary solution containing 80 mL of anhydrous ethanol and 80 mL of deionized water. Next, different masses of AgNO$_3$·5H$_2$O (0 g, 0.026 g, 0.078 g, 0.13 g, corresponding to Ag/Sn ratios of 0, 1, 3 and 5 at.%) was added to the above mentioned solution. Then, the mixture was continuously stirred at constant temperature for 30 min to prepare a homogeneous precursor solution. The mixed precursor solution was transferred into a 200 mL Teflon lined stainless steel autoclave and heated at 180 °C for 20 h. After the sample was cooled to room temperature, the sample was washed four times with deionized water and absolute ethanol to remove impurity respectively. The samples were finally obtained after air dried at 80 °C for 24 h.

2.3. Characterization of the Sensing Materials

The phase of the resultant powders were investigated by X-ray diffraction (XRD, D/Max-1200X, Rigaku, Tokyo, Japan) with Cu-Ka radiation ($\lambda = 1.54178$ Å), and the scanning speed was 0.02° s$^{-1}$ for 2θ in the range of 20°–80°. The morphology of resultant powders was performed with field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Tokyo, Japan). The elemental composition of the obtained samples was analyzed using energy dispersive spectroscopy (EDS, Oxford INCA 250, JEOL, Tokyo, Japan) and X-ray photoelectron spectroscopy (XPS, KRATOS X SAM800, Kratos, Manchester, Kingdom).

2.4. Fabrication and Measurements of the Sensing Devices

In the present experiment, sensing devices were fabricated with the side heated structure. The as-prepared powders were mixed with suitable amount of anhydrous ethanol and deionized
water (with 8:1:1 ratio) to form a homogeneous paste, which was coated evenly onto a prefabricated alumina tube attached with a pair of gold electrodes and platinum wires to form a film, then dried at room temperature and subsequently calcined at 500 °C for 4 h (Figure 1a). Next a Ni–Cr heating wire was inserted in the tube to form an inside heated sensing device (Figure 1b). Finally, the sensing devices were placed on the aging instrument of the side heat sensor at 120 °C for 10 days to improve the stability of the components. The gas sensing properties of the fabricated sensing devices were measured by a CGS-8 (Chemical gas sensor-8, Beijing Elite Tech Co., Ltd., Beijing, China) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., Beijing, China). The gas sensor response was defined as $R_a/R_g$, where $R_a$ and $R_g$ were the resistance of the sensor in air and in the test gas, respectively [25].

![Figure 1. Schematic diagram of (a) ceramic tube and (b) the indirect-heating sensor.](image)

3. Results and Discussion

3.1. Materials Characterization

Figure 2 shows the XRD patterns of pure and 1 at.%, 3 at.%, 5 at.% Ag-doped SnO$_2$ nanospheres. It can be found that the XRD patterns of the samples are smooth and the shape of the peak is sharp, indicating that the prepared samples have well developed to crystal grains and showed good crystallization performance. As shown in Figure 2a, all the diffraction peaks can be readily indexed to the tetragonal phase of rutile SnO$_2$ structure, good agreement with the reported values (JCPDS card No. 41-1445) without any other phase detected, indicating that pure SnO$_2$ has been obtained [26]. The XRD patterns of 1 and 3 at.% Ag-doped SnO$_2$ shows almost no change compared with that of the pure SnO$_2$ products, which may be due to the poor amount of Ag in the Ag-SnO$_2$ nanospheres [27]. Moreover, the diffraction peaks labeled as (111) and (200) in Figure 2d is observed, which can be indexed to the face centered cubic phase of Ag nanoparticles (JCPDS card No. 04-0783).

![Figure 2. XRD patterns of pure and 1 at.%, 3 at.%, 5 at.% Ag-doped SnO$_2$.](image)
The crystallite sizes \( d \) of the pure \( \text{SnO}_2 \) and 5 at.% Ag-doped \( \text{SnO}_2 \) nanomaterials were measured by the well-known Debye-Scherer equation (Equation (1)).

\[
d = \frac{0.89\lambda}{\beta \cdot \cos \theta}
\]

where \( \lambda \) is the X-ray wavelength and has a value of 1.542 Å, \( \theta \) is the Bragg diffraction angle and \( \beta \) is the full width at half maximum (FWHM). For estimating the crystallite size of pure and Ag-doped \( \text{SnO}_2 \) nanomaterials accurately, the three most intense peaks corresponding to (110), (101) and (211) diffraction planes were calculated and shown in Table 1. The average crystallite size of the pure and 5 at.% Ag-doped \( \text{SnO}_2 \) were found to be 4.38 nm and 4.07 nm, respectively.

**Table 1.** Different XRD parameters for the determination of crystallite sizes.

| Nanomaterials   | (hkl) | 2Theta (°) | FWHM (β) | Crystallite Size (nm) |
|-----------------|-------|------------|----------|-----------------------|
| Pure \( \text{SnO}_2 \) | (110) | 26.48 | 2.1 | 3.85 |
|                 | (101) | 33.98 | 1.75 | 4.69 |
|                 | (211) | 51.78 | 1.9 | 4.60 |
| 5 at.% Ag-\( \text{SnO}_2 \) | (110) | 26.58 | 2.3 | 3.51 |
|                 | (101) | 33.88 | 1.95 | 4.22 |
|                 | (211) | 51.88 | 1.95 | 4.48 |

As shown in Figure 3, the size distribution and the morphology of the as-prepared pristine and Ag-doped samples were analyzed by FESEM. All the samples are nearly spherical structure and the diameters of all microspheres are in the scope of 80 to 120 nm. Moreover, good dispersion of all samples is also observed. The FESEM images indicate that the doping does not change the morphology and surface structure of \( \text{SnO}_2 \) samples.

![Figure 3. FESEM images of (a) pure; (b) 1 at.%; (c) 3 at.%; and (d) 5 at.% Ag doped \( \text{SnO}_2 \).](image-url)
In order to check whether metallic Ag was successfully doped into the SnO$_2$ nanomaterials, EDS measurements were performed, and the EDS spectra of the pure and 3 at.% Ag-doped SnO$_2$ are shown in Figure 4a,b, respectively. As shown in Figure 4a, only Sn and O peaks are observed for SnO$_2$, indicating that as-prepared SnO$_2$ is of high purity. The strong signals of elemental Sn, O and a weak signal of Ag are detected in Figure 4b, which indicates that the prepared SnO$_2$ nanomaterials are successfully doped with Ag and the atomic percent of Ag is calculated to be about 2.98 at.%.

![Figure 4. EDS spectra of (a) pure (b) 3 at.% Ag-doped SnO$_2$ nanospheres.](image)

For further analyzing the elemental composition of the obtained samples and the valence of each element, XPS tests were investigated. The XPS spectrum of the synthesized 3 at.% Ag-doped SnO$_2$ nanospheres is represented in Figure 5a, where spectra from Sn, O and Ag elements are observed and the Ag atom concentrations in the composites is 2.98 at.%. In order to further investigate the existence state of Sn, O and Ag in the prepared materials, the enlarged XPS survey spectra of Sn 3d, O 1s, Ag 3d are showed in Figure 5b–d, respectively. Figure 5b,c show the binding energy of Sn 3d$_{5/2}$, Sn 3d$_{3/2}$ and O 1s are 486.85 eV, 495.35 eV and 530.59 eV respectively, which are the confirmatory peaks for a Sn$^{4+}$ and O$^{2-}$ ions of SnO$_2$ and in good accordance with the standard parameter values [28]. As shown in Figure 5d, the Ag 3d spectrum exhibits doublets of Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ at 368.21 eV and 374.19 eV, which correspond to the state of metallic silver [29].

![Figure 5. XPS survey spectra of 3 at.% Ag-doped SnO$_2$ nanospheres (a) full; (b) Sn 3d; (c) O 1s; (d) Ag 3d.](image)
3.2. Hydrogen Gas Sensing Studies

In order to investigate the optimal operating temperature of the fabricated sensors to detect H₂, the gas sensing responses of the pure and Ag-doped SnO₂ towards 50 µL/L of H₂ gas were measured respectively, with operating temperatures ranging from 150 °C to 480 °C. As shown in Figure 6, with the increase of the temperature, the sensing response of all the prepared sensors increases at first and attains a maximum value at a particular temperature. Then it decreases with further increase of temperature. The operating temperature could be taken as a balance between two processes adsorption and desorption [30]. When the temperature is larger than the particular value, the adsorption of oxygen becomes increasingly inefficient and the active oxygen species reduces in quantity, so the gas response begins to decline. When exposed to 50 µL/L H₂, the measured optimal operating temperature of the 1 at.% , 3 at.% and 5 at.% Ag-doped SnO₂ sensors is 300 °C with the corresponding response of 8.61, 25.25 and 15.78, respectively. The notable difference of responses between pure and Ag-doped SnO₂ can be attributed to the catalytic activity of Ag [31]. As comparison, the response of the fabricated pure SnO₂ for 50 µL/L H₂ at operating temperature of 360 °C is 5.04, which is lower than those of Ag-doped SnO₂. It could be explained that Ag doping influences the shift of optimal operating temperature towards lower temperature due to a decrease in the band gap [27]. The 3 at.% Ag-doped SnO₂ sensor exhibits the highest H₂ gas response among the four sensors. The decrease of response for the doped sensor above 3 at.% Ag is observed, possibly due to the reduction of active sites associated with the agglomeration of Ag nanoparticles [32].

![Figure 6](image_url)

Figure 6. Gas responses of pure, 1 at.%, 3 at.% and 5 at.% Ag-doped SnO₂ based sensor to 50 µL/L H₂ at different working temperature.

In order to explore the relation between response and the concentration of H₂, experiments of responses of pure and Ag-doped SnO₂ sensors to various concentration of H₂ (from 1 µL/L to 2000 µL/L) are conducted at their own optimum operating temperature and the results are presented in Figure 7. It is apparent that the response of above samples increases rapidly within 1–500 µL/L H₂ gas concentration and then slows down so that it converges to a constant. It can be known that the sensors are almost at saturation when the concentration of H₂ above 1000 µL/L. Compared with the other three sensors, the 3 at.% Ag-doped SnO₂ sensor exhibits the highest response towards certain concentration of H₂ gas, which might be attributed to the appropriate incorporated of Ag nanoparticles [33]. Obviously, the gas response exhibits a linear relationship with gas concentration when the latter ranges from 1 to 50 µL/L (inset of Figure 7), indicating that the sensors suit well for low concentration detection.
Figure 7. Gas responses of pure, 1 at.%, 3 at.% and 5 at.% Ag-doped SnO$_2$ based sensor versus different concentration of H$_2$ under their optimum operating temperature. (a) Pure; (b) 1 at.% Ag-doped SnO$_2$; (c) 3 at.% Ag-doped SnO$_2$; (d) 5 at.% Ag-doped SnO$_2$.

It is significant that the sensor has a swift response and rapid recovery time in the real time fast changing environment. Response and recovery times of gas sensors are usually defined as the time required while reaching 90% of the final resistance in the case of the process of adsorption and desorption, respectively. Figure 8 shows response-recovery behavior of the pure, 1 at.%, 3 at.% and 5 at.% Ag-doped SnO$_2$ sensors to 50 µL/L of H$_2$ gas at their own optimum operating temperature. The response and recovery times for the pure, 1 at.%, 3 at.% and 5 at.% Ag-doped SnO$_2$ sensors of 50 µL/L H$_2$ are 26–34 s, 22–28 s, 10–17 s and 18–25 s, respectively. It proves that the 3 at.% Ag-doped SnO$_2$ sensor has better sensing performance.

Figure 8. Response-recovery curves of the as-prepared sensors to 50 µL/L H$_2$ at their own optimum operating temperature: (a) pure SnO$_2$ sensor; (b) 1 at.% Ag-doped SnO$_2$ sensor; (c) 3 at.% Ag-doped SnO$_2$ sensor; (d) 5 at.% Ag-doped SnO$_2$ sensor.
Figure 9 depicts the response-recovery curve of the 3 at.% Ag-doped SnO$_2$ sensor to H$_2$ in a range of 10–100 µL/L under its optimum working temperature. Clearly, the as-prepared sensor exhibit a rapid response-recovery times, and its can recover with the nearly initial values after many cycles between exposure to H$_2$ and air.

![Figure 9. Dynamic response-recovery curve of the 3 at.% Ag-doped SnO$_2$ sensor to H$_2$ in a range of 10–100 µL/L under its optimum working temperature.](image)

The stability of the fabricated pure, 1 at.%, 3 at.% and 5 at.% Ag-doped SnO$_2$ to 100 µL/L H$_2$ at their optimum temperatures was investigated every 20 days for total 160 days. Figure 10 shows the response variation curves and it is obvious that the responses changed very slightly. Therefore, a good stability of the sensors was conformed.

![Figure 10. The long-term stability of pure, 1 at.%, 3 at.% and 5 at.% Ag-doped SnO$_2$ to 100 µL/L H$_2$ at their optimum temperatures.](image)

3.3. Hydrogen Sensing Mechanism

It is well known that the gas sensing mechanism of SnO$_2$ gas sensor belongs to the surface-controlled type, and the gas sensing performance is highly dependent upon the surface reactions between the target gas and adsorbed oxygen species on the surface area of SnO$_2$ [34]. Figure 11 illustrates the schematic diagram for sensing mechanism of the H$_2$ sensors based on pure and Ag-doped SnO$_2$ nanomaterials, where $E_F$, $E_c$ and $E_v$ denote Fermi level, conduction band and valence band, respectively. When pure SnO$_2$ gas sensor is exposed to air (Figure 11a), oxygen molecules can be adsorbed on the sensor surface and capture electrons from the conduction band of SnO$_2$ to generate chemisorbed oxygen species ($O^-$, $O_2^-$ and $O^2-$), which results in a depletion layer on the surface and the decreasing electrical conductivity of sensing materials [35–37]. When SnO$_2$ sensing materials are
exposed to H$_2$ (Figure 11b), H$_2$ gas interacts with the adsorbed oxygen species, and then the trapped electrons are released back into the conduction band of SnO$_2$, thereby increasing its conductivity.

Compared with the pure SnO$_2$, the Ag-doped SnO$_2$ composite sensing materials exhibit enhanced gas sensing properties, which might be ascribed to the following aspects. Firstly, as we know, the work function of Ag (4.72 eV) is higher than that of SnO$_2$ (4.60 eV), and the Schottky junctions would form between Ag and SnO$_2$, which causes electrons transfer from SnO$_2$ to Ag [38]. Thus, a depletion region would be formed in SnO$_2$ near the interface of Ag and SnO$_2$ [39,40]. Secondly, Ag nanoparticles can act as active site to reduce the reaction barrier between H$_2$ and the adsorbed oxygen species due to its good catalytic ability, which results in a further extend in width of the depleted layer [23]. In addition, Ag nanoparticle has a tendency to form Ag$_2$O in the air and Ag$_2$O is a kind of p type semiconductor that will further intense electron depletion layer on the sensors surface [27,41]. Meanwhile, as shown in Figure 11e,f, the presence of Ag nanoparticle favors the gas sensing response by the process of chemical sensitization, catalytic oxidation (spill-over effect), resulting in increasing the quantities of active oxygen species on the surface of the Ag-doping SnO$_2$ nanocomposite [34,42]. Thus, the resistance of the Ag-doped SnO$_2$ gas sensors become significantly larger than that of pure SnO$_2$ sensor in air (Figure 11c). When the sensor is exposed to H$_2$ (Figure 11d), the thick electron depletion layer would decrease sharply to a thin layer by the reaction of H$_2$ and adsorbed oxygen species, leading to a significantly enhanced gas response [43,44]. Table 2 compares the H$_2$ sensing performances of the fabricated 3 at.% Ag-doped SnO$_2$ nanospheres based sensor with the different sensors reported in the literature. The presented Ag-SnO$_2$ nanospheres exhibited comparatively better gas response with low response and recovery times.

**Figure 11.** The sensing mechanism of pure and Ag-doped SnO$_2$: (a) pure SnO$_2$ in air; (b) pure SnO$_2$ in H$_2$ gas; (c) Ag-doped SnO$_2$ in air; (d) Ag-doped SnO$_2$ in H$_2$ gas; (e) active oxygen distribution of pure SnO$_2$; (f) active oxygen distribution of Ag-doped SnO$_2$.  

M$\text{at}$$\text{e}r$$\text{i}$$\text{a}$$\text{l}$$\text{s}$$ \text{20}\text{18, 11, 492} $
4. Conclusions

In summary, Ag-doped SnO\textsubscript{2} nanospheres with different atomic percent (pure, 1 at.% and 5 at.%) have been successfully synthesized by a hydrothermal process for the fabrication of highly sensitive H\textsubscript{2} sensing devices. The crystalline structures and morphologies of as-prepared nanomaterials were characterized via XRD and FESEM, proving the microspheres nanostructures. The EDX and XPS patterns verified the element components and valences, and the standard peaks of metallic silver were obviously observed. The gas sensing properties of prepared nanomaterials have been investigated. The main characteristics of the fabricated Ag-doped SnO\textsubscript{2} sensor are wide range of H\textsubscript{2} response (1–2000 μL/L), lower temperature operation, quick response recovery times, as well as good stability over time. Gas sensing results demonstrate that the obtained 3 at.% Ag-doped SnO\textsubscript{2} sensor shows the best hydrogen sensing performance at 300 °C, suggesting that the moderate Ag-doped SnO\textsubscript{2} sensor is highly promising for H\textsubscript{2} sensing application.

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Table 2. Summary of the H\textsubscript{2} gas sensing performances of different gas sensor materials.

| Sensing Material | Concentration | Temp. (°C) | Response | Response Formula | Response Time (s) | Recovery Time (s) | Ref. |
|------------------|---------------|------------|----------|------------------|-------------------|-------------------|-----|
| Pd-SnO\textsubscript{2}/MoS\textsubscript{2} | 5000 ppm | K.T. | 18% | (R\textsubscript{a} - R\textsubscript{g})/R\textsubscript{a} × 100% | 50 | 19 | [14] |
| Pt/SnO\textsubscript{2} | 500 ppm | 110 | 168 | (R\textsubscript{a} - R\textsubscript{g})/R\textsubscript{a} × 100% | <6 | 57 | [30] |
| WO\textsubscript{3}/SnO\textsubscript{2} | 2000 ppm | 225 | 52.39 | R\textsubscript{a}/R\textsubscript{g} | 6.6 | - | [45] |
| Au/SnO\textsubscript{2} | 5000 ppm | 400 | 50 | R\textsubscript{a}/R\textsubscript{g} | 25 | 170 | [46] |
| CeO\textsubscript{2}/SnO\textsubscript{2} | 0.5 ppm | 300 | -82 | R\textsubscript{a}/R\textsubscript{g} | -50 | -30 | [47] |
| Ag/SnO\textsubscript{2} | 50 μL/L | 300 | 25.25 | R\textsubscript{a}/R\textsubscript{g} | 10 | 17 | This work |
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