Hydrothermally Synthesized CeO$_2$ Nanowires for H$_2$S Sensing at Room Temperature

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Abstract

CeO$_2$ nanowires were synthesized using a facile hydrothermal process without any surfactant, and their morphological, structural and gas sensing properties were systematically investigated. The CeO$_2$ nanowires with an average diameter of 12.5 nm had a face-centered cubic fluorite structure and grew along [111] of CeO$_2$. At the room temperature of 25 °C, hydrogen sulfide (H$_2$S) gas sensor based on the CeO$_2$ nanowires showed excellent sensitivity, low detection limit (50 ppb), and short response and recovery time (24 s and 15 s for 50 ppb H$_2$S, respectively).

Keywords: CeO$_2$, Nanowires, Hydrothermal, Sensitivity, Gas sensor

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1 Introduction

Cerium oxide (CeO$_2$) based nano-material, one of multi-functional n-type semiconductor materials, have attracted great attention recently because of its superior catalytic performance [1-5], optical properties [6-8], oxygen storage capacity [9], and magnetic properties [10-12]. Therefore, it has been widely used in the field of catalyst [1-3], photocatalyst [4-5], solid oxide fuel cells [6-7], oxygen pump [9] and luminescence materials [13-15]. Recently, CeO$_2$ has also been proposed for one potential sensing material in the field of solid state gas sensors for environmental monitoring, such as CO [16,17], CH$_4$ [17], O$_2$ [18], NO$_2$ [19], carbon disulfide [20] and humidity [21]. Nanostructured CeO$_2$ could significantly enhance the gas sensing performance because of its characteristic structural and electronic properties as mentioned above. It is generally accepted that increasing surface area to volume ratio and decreasing crystal sizes of the CeO$_2$ are crucial to achieve a highly sensitive gas sensors [21]. Apart from crystal size, different crystal structures and surface morphologies of the CeO$_2$ nanomaterials could affect their physical and chemical properties and provide new functions for applications. Recently, one-dimensional (1D) CeO$_2$ nanostructures have attracted great attention. Much effort has been made on the fabrication of 1D CeO$_2$ nanowires using electrochemical assembly [6,22], electro-spinning [23], precipitation [24-25], and hydrothermal method [4,26-30]. Compared with other preparation methods to synthesize the CeO$_2$ nanostructures, hydrothermal methods have advantages of low synthesis temperature and no need for post-sintering. Most of the current synthesis approaches to grow the hierarchical
architectures (including 1D nanostructure) require templates or surfactants, or complicated procedures [27-28]. It remains a challenge to develop facile and effective template-free methods for 1-D CeO$_2$ nanostructures with various properties and applications. The gas sensor based on the 1-D CeO$_2$ nanostructures to detect the H$_2$S has never been reported.

This paper reported a hydrothermal process to prepare CeO$_2$ nanowires without using any template or surfactant. The gas sensor for detecting H$_2$S at room temperature was fabricated and characterized using the CeO$_2$ nanowires.

2. Experimental procedures

2.1 Synthesis and characterization

Ce(NO$_3$)$_3$·9H$_2$O, urea and NaOH of analytical grade were purchased from Sinopharm Chemical Reagents Co., Ltd (Shanghai, China) and used as received without any further purification. De-ionized water with a resistivity of 18.0 MΩ·cm was used throughout the synthesis process. The CeO$_2$ nanowires were synthesized using a hydrothermal reaction method. In a typical synthesis process, a mixed solution was prepared by dissolving NaOH (40.0 g) and urea (15.0 g) into 100 ml deionized water. Then, 10 ml Ce(NO$_3$)$_3$·6H$_2$O solution (0.5 mol/L) was slowly dripped into the mixed solution under continuously stirring to form a suspension. The suspension was stirred for 30 minutes and then transferred into a 150 mL Teflon-lined stainless steel autoclave for a hydrothermal reaction at 100 °C for 24 hours. After that, the product was cooled down to room temperature, centrifuged, washed with deionized water and anhydrous ethanol for three times. Finally, it was dried in air at 70 °C for 10 hours to
obtain the CeO$_2$.

Crystalline phases of the CeO$_2$ nanowires were determined using X-ray diffraction (XRD, CuK$_\alpha$, 40kV, 60mA, Rigaku D/max-2400). The morphologies were observed using scanning electron microscopy (SEM, Inspect F50, USA). High resolution transmission electron microscope (HRTEM, JEM-2200FS, Japan) was used to characterize crystallographic features of the sample. The specific BET (Brunner–Emmet–Teller) surface areas of the CeO$_2$ nanostructures were measured using nitrogen adsorption isotherm at 77 K (Tristar3000, Micromeritics). The chemical state of CeO$_2$ nanostructures was determined using a KRATOS XSAM 800 X-ray photoelectron spectrometer (XPS) with monochromatic AlK$_\alpha$ (h$_\nu$ = 1486 eV) radiation. Diffuse reflectance spectrum (DRS) was recorded using a Shimadzu UV-2101 apparatus, equipped with an integrating sphere, using BaSO$_4$ as the reference.

2.2 Gas sensor fabrication and measurement

Gas-sensing performance of the device was evaluated using a WS-30A gas sensor measurement system (Weisen Electronic Technology Co., Ltd., Zhengzhou, China) at the room temperature of 25 °C. Fabrication processes of the gas sensor are as follows: (i) the as-prepared CeO$_2$ nanowires were mixed with absolute ethyl alcohol with a weight ratio of 1:4 and then ultrasonically agitated for 15 min until the formation of a homogeneous slurry; (ii) the slurry was pasted onto an alumina tube; (iii) the CeO$_2$ coated alumina tube was calcined at 300 °C for 2 hours to improve the stability of the sensor and remove the residual organics on the surface of sensor. Fig. 1a shows the
schematic illustration of the gas sensor, where a Ni-Cr heater was placed inside the alumina tube as a resistor to control the working temperature of the sensor. A pair of gold electrodes were connected onto the alumina tube, and two Pt wires have been used to form measurement circuit for resistance measurements. Fig. 1b displays a measurement circuit of the gas sensor, where $R_E$ is a load resistor connected in series with the gas sensor, and $R_S$ donates the resistor of the sensor. During sensing testing, an appropriate working voltage ($V_s=5$ V) was applied and the response of the sensor was monitored from the voltage changes of the $R_E$. The gas response ($S$) is defined as:

$$S = \frac{R_a}{R_g},$$

where the $R_a$ and $R_g$ are the resistances values from the sensor measured in air and the target $H_2S$ gas, respectively.

Fig.1 (a) Schematic of the gas sensor based on CeO$_2$ nanowires sensing materials, (b) The measurement electric circuit for the gas sensor.

3. Results and discussion

3.1 Structural and morphological characteristics

Fig. 2 shows the XRD spectrum of the as-prepared CeO$_2$ nanowires sample. The characteristic diffraction peaks corresponded to the (111), (200), (220), (311), (222), (400), (311) and (420) planes of a face-centered cubic fluorite structure of CeO$_2$ (with
a lattice constant of \(a = 0.5411 \text{ nm}\) according to JCPDS file 34-0394). No obvious peaks corresponding to cerium nitrate or other types of cerium oxides were identified from the XRD results, indicating that the sample is pure CeO\(_2\).

![XRD spectrum of CeO\(_2\) nanowires](image)

**Fig. 2** XRD spectrum of CeO\(_2\) nanowires

![SEM, TEM, HRTEM, and SAED images](image)

**Fig. 3** (a) SEM image (inset indicates the size distribution histogram of diameter of nanowires), (b) TEM image, (c) HRTEM image and (d) the selected area electron diffraction pattern (SAED) of the obtained CeO\(_2\) sample.
Fig. 3a and Fig 3b display the SEM and TEM images of the obtained CeO$_2$ sample, respectively. A large quantity of nanowires with an average diameter of 12.5 nm are clearly seen, and there are also a small amount of nanoparticles with an average diameter of about 8.0 nm. Fig. 3c shows the HRTEM image of the individual CeO$_2$ nanowires, revealing that they are structurally uniform and single crystalline in nature. The growth direction of the CeO$_2$ nanowires is along [111]. The lattice fringes in Fig. 3c illustrate two interplanar spacing values, i.e., 0.312 and 0.271 nm, which are consistent with the (111) and (200) planes of the CeO$_2$, respectively. There are some defects on the surface of CeO$_2$ nanowires (see the area in red circle), which could provide more reaction centers for the gas sensing. The crystalline nature of the resultant CeO$_2$ nanowires could be verified by the selected area electron diffraction (SAED) pattern (Fig. 3d) which is basically a ring pattern. The diffraction rings in the pattern can be indexed to (111), (200), (220), (311), (331) and (420) planes of the crystalline face-centered cubic structure, which is consistent with the XRD spectrum.

It is well-known that the Ce(III) oxidation state is unstable compared with the Ce(IV) oxidation state in alkaline solution [31]. In the experiment, Ce$^{3+}$ oxidation state resulted in the formation of hydrated Ce$^{4+}$ oxide as shown below:

$$4\text{Ce}^{3+} + 12\text{OH}^- + \text{O}_2 + (4n-6)\text{H}_2\text{O} \rightarrow 4(\text{CeO}_2\cdot n\text{H}_2\text{O})$$  \hspace{1cm} (1)

In the hydrothermal process, urea could yield NH$_3$ and CO$_2$ through controlled hydrolysis in aqueous solutions (Equation (2)), i.e.:

$$\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3$$  \hspace{1cm} (2)
It is clear that the NH$_3$ played an important role for nanowire growth. After the initial nucleation, the monomers would grow into CeO$_2$·H$_2$O nanoparticles, and the NH$_3$ gas bubbles would be absorbed on its surface. In the present reaction system, microbubbles of NH$_3$ provided a bridge-linking role for the aggregation of these nanoparticles. Nanoparticles might aggregate around the gas–liquid interfaces between the NH$_3$ and water to form CeO$_2$·H$_2$O nanowires. With the prolonging of the hydrothermal reaction, the CeO$_2$·H$_2$O was crystallized and transformed into CeO$_2$ at an elevated temperature of 100 °C, i.e.:

$$\text{CeO}_2\cdot\text{nH}_2\text{O} \rightarrow \text{CeO}_2 + \text{nH}_2\text{O}$$  \hspace{1cm} (3)

Using the analysis from the BET surface area, the obtained specific surface area of the as-deposited CeO$_2$ nanowires were 86.0 m$^2$·g$^{-1}$. The nano-size diameters and large surface areas of CeO$_2$ nanowires are suitable for gas sensing.
Fig. 4 XPS spectra of CeO$_2$ nanowires: (a) Ce 3d, (b) O 1s, (c) S before and after exposure to H$_2$S.

Fig. 4 shows the Ce 3d and O 1s XPS spectra of the CeO$_2$ nanowires. The Ce 3d spectrum (see Fig. 4a) shows six peaks resulting from three pairs of spin–orbit splits with different state configurations of 4f ($i = 0, 1, 2$). The peaks located at around 882.8 eV, 888.1 eV and 898.4 eV are assigned to the Ce 3d$_{5/2}$, and those at around 901.3 eV, 907.0 eV and 916.7 eV are assigned to the Ce 3d$_{3/2}$. The high binding energy of 916.9 eV and 898.4 eV are assigned to the final state of Ce(IV) 3d$^4$4f$^0$O2p$^6$. The peaks at 907.5 eV and 888.9 eV are assigned to the hybridization state of Ce(IV) 3d$^6$4f$^4$O2p$^5$, and those at 901.0 eV and 882.3 eV assigned to the state of Ce(IV) 3d$^6$4f$^2$O2p$^4$ [32, 33]. It is obvious that the samples are in the state of Ce$^{4+}$ without any impurity of the Ce$^{3+}$ state. The XPS O 1s spectrum (Fig. 4b) is asymmetric and deconvoluted into 529.3 eV and 531.9 eV, respectively. The peak at 529.3 eV is assigned to the oxygen located in the CeO$_2$ crystal lattice [33], and that at around 531.9 eV is assigned to hydroxyl groups on the surface of CeO$_2$. Clearly there are large numbers of hydroxyl groups on the CeO$_2$ surface according to the high peak intensity, which might result in a high electrochemical activity. Fig. 4c shows the XPS spectra of CeO$_2$ nanowires before and after exposure to 100 ppm H$_2$S gas. It can be seen that a signal of S element appeared after it was exposed to H$_2$S, indicating that the adsorption of H$_2$S on the surface of CeO$_2$ nanowires.
The UV-Vis diffuse reflectance spectrum of the CeO₂ nanowires is shown in Fig. 5. The spectrum exhibits a strong absorption band at the UV region due to the charge-transfer transitions from O 2p to Ce 4f bonds, which can be explained based on the well-known f to f spin-orbit splitting of the Ce 4f state [31]. The absorbing band edge is at 405.2 nm, which meant that the estimated direct band gap energy was 3.06 eV for the CeO₂ nanowires.

### 3.2 Gas sensing properties

Fig. 6 I-V characteristics between the two electrodes bridged by the CeO₂ nanowires
film at room temperature

Fig. 6 plots a typical current-voltage (I-V) curve between the two electrodes bridged by the CeO$_2$ nanowires at room temperature. The current increases linearly with the applied bias voltage (from $-10$ V to $10$ V). Such a linear behavior reveals that a good ohmic contact was established between the CeO$_2$ nanowires and two electrodes. In addition, the I-V curve is non-hysteretic, indicating that the wire to wire connectivity is fairly good. The resistance of the nanowires film calculated from the slope of the curve is 172.0 MOhm.

![Fig. 6](image)

Fig. 7 (a) Dynamic response-recovery curve and (b) response sensitivity of the CeO$_2$ nanowires based sensor to H$_2$S gas with different concentrations at room temperature.

Fig. 7a shows the response-recovery curves of the sensor exposed to different concentrations of H$_2$S gas at room temperature. For all the measurements in the dry air, the gas sensor showed a constant and stable baseline. When the H$_2$S gas was introduced into the chamber, the resistance of the gas sensor underwent a quick decrease. However, when the chamber was refilled with the dry air, it was also quickly recovered to its original baseline. It is in a good agreement with the sensing
mechanism of n-type semiconductor gas sensor [16]. After several cycles of gas injection and air purging alternatively, a full recovery to the initial readings was achieved, indicating a good reversibility of the gas sensor at room temperature. The response sensitivity of the gas sensor to the H₂S (from 0.05 to 100 ppm) was calculated and the results are shown in Fig. 7b. The response sensitivity increased with the increasing concentration of the H₂S, and it showed a good response to the low concentration ranges of sub-ppm level. The sensor showed a significant response to the concentration as low as 50 ppb with the response value of 1.11, indicating that the gas sensor has a good sensitivity at room temperature.

CeO₂ is an n-type metal oxide semiconductor and its sensing performance is determined by the changes of the resistance which are resulted from the chemical reactions between the testing gases and the oxygen species adsorbed on the surface of the sensor [34,35]. When the CeO₂ nanowires based sensors are exposed to the air, the oxygen molecules are absorbed on the surface of the CeO₂ nanowires. Negatively charged chemisorbed oxygen species are formed by extracting electrons from conduction band of the CeO₂ nanowires which causes a decrease in conductivity of the sensor. Consequently, an electron-depletion layer is formed on the surface [36,37]. The types of absorbed oxygen species are dependent on the working temperature. At room temperature, O₂⁻ is commonly chemisorbed on the surfaces of the CeO₂ nanowires [38]. The detail reaction at room temperature could be described as follows:

\[ \text{O}_2(g) \rightarrow \text{O}_2(ad) \]  \hspace{1cm} (4)
When the sensor is exposed to the H$_2$S gas, the H$_2$S molecules are adsorbed onto the surfaces of the CeO$_2$ nanowires. Because the CeO$_2$ have strong redox capability, it was in favor of the redox reaction of H$_2$S gas on the surface of CeO$_2$[1-3]. They will react with the previously absorbed oxygen species (O$_2^-$) and generate sulfur oxides and H$_2$O vapor. The reaction between the H$_2$S gas and absorbed oxygen species could be expressed using the following equation [38,39]:

$$2\text{H}_2\text{S} + 3 \text{O}_2^-(\text{ad}) \leftrightarrow 2\text{H}_2\text{O(g)} + 2\text{SO}_2(g) + 3 \text{e}^-$$

(6)

During this process, the electrons will be released into the conduction band of the CeO$_2$ nanowires. As the result, the thickness of the electron-depletion layer is reduced and the resistance of the CeO$_2$ nanowires decreases as well.

According to the sensing mechanisms of the semiconductors [36-39], the good H$_2$S sensing performance of the CeO$_2$ nanowires is related to the following factors. Firstly, the diameter of the crystalline nanowires is less than 12.5 nm, and the surface area of the nanowires is significantly large. Therefore, the size effect is favorable for the good sensing performance of the nanowires. Secondly, the good sensing performance may be attributed to the fact that there are some defects on the surfaces of CeO$_2$ nanowires (see the Fig. 3c), which could provide the extra reaction sites during the gas sensing.

The response and recovery time were defined as the time to reach 90% of the maximum sensing response upon injecting of testing gas and the time to reach 10% of
the maximum sensing response upon purging with dry air. Fig. 8 shows the response and recovery time of the CeO$_2$ nanowires based gas sensor at different H$_2$S gas concentrations. The gas sensor showed a fast response and the recovery time of less than 100 s and 260 s for different concentrations. In addition, at the low concentration below 1 ppm, the response and the recovery time were about 50 s and 20 s, respectively. The fast response and recovery are attributed to the smaller size diameter, larger surface area and more defects on the surface of CeO$_2$ nanowires, which are all beneficial for the fast absorption and desorption of the H$_2$S molecules. It should also be mentioned that the response time showed only little variation upon exposed to different concentrations of the H$_2$S gas. Because the desorption of H$_2$S molecules became slow at a higher concentration of the H$_2$S gas, the recovery time increased obviously with increasing the H$_2$S concentration from 10 to 100 ppm.

![Graph showing response and recovery time of the CeO$_2$ nanowires based sensor to H$_2$S gas at room temperature.](image)

Fig. 8 Response and recovery time of the CeO$_2$ nanowires based sensor to H$_2$S gas at room temperature.

Reproducibility of the sensor was demonstrated by successively exposing it to the H$_2$S gas at a concentration of 100 ppm for 5 cycles at room temperature, and the
results are shown in Fig. 9a. During the repeated gas injection and purging with dry air in the five consecutive sensing cycles, the response-recovery curves of the sensor are almost identical. From the data of the long-term stability shown in Fig. 9b, the largest deviation of the response sensitivity is less than 5% after continuous sensing testing for 20 days, indicating that the sensor possesses an excellent reproducibility and long-term stability for the H$_2$S detection.

Fig. 9 (a) Response-recovery curve of the gas sensor to 100 ppm H$_2$S gas for 5 cycles, (b) Long-term stability of the gas sensor to 100 ppm H$_2$S gas for 20 days at room temperature.

Fig.10 Selectivity histogram of the CeO$_2$ nanowires based sensor toward difference gases (C$_2$H$_5$OH, CO, H$_2$, NH$_3$ and H$_2$S) at the same concentration of 100 ppm.
The responses of the gas sensor to several types of the reducing gases (C$_2$H$_5$OH, CO, H$_2$, NH$_3$ and H$_2$S) were measured with the same gas concentration of 100 ppm at room temperature. The results are shown in Fig. 10. The inset in the Fig. 10 shows the response curves when the sensor was exposed to the different target gases. Clearly, the sensor displays remarkably higher response to the H$_2$S gas compared those to the other gases at the same testing conditions. As is shown in Fig. 10, the responses to C$_2$H$_5$OH, CO, H$_2$, NH$_3$ with the same concentration was 1.25, 1.23, 1.15 and 1.19, respectively. These data, which are far less than that to the H$_2$S gas at the same concentration of 1.98, suggesting that the sensor has a good selectivity toward H$_2$S gas.

4. Conclusions

In summary, based on a facile hydrothermal process without using any template or surfactant, the CeO$_2$ nanowires were successfully synthesized without further heat treatment. The CeO$_2$ nanowires are uniform with an average diameter of 12.5 nm. The nanowires were single crystalline with a preferred orientation along [111]. At room temperature, the CeO$_2$ nanowires based on gas sensor showed good sensitivity, rapid response/recovery time, low detection limit, long term stability and good selectivity towards H$_2$S, indicating that the CeO$_2$ nanowires prepared by this method can be a promising sensing material for fabrication high-performance H$_2$S gas sensor.

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