Gadolinium-Doped CeO$_2$ Gas Sensor for H$_2$S Sensing

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Abstract: Dihydrogen sulfide (H$_2$S) gas has a flammable nature and is one of the most toxic and dangerous gases. Even small concentrations can be fatal to humans. Herein, we investigated the H$_2$S gas-sensing features of commercial pristine cerium oxide (CeO$_2$) and gadolinium (Gd)-doped CeO$_2$ (GDC) nanoparticles. First, the sensing materials were well-characterized using various methods including X-ray photoelectron spectroscopy, transmission electron microscopy and X-ray diffraction to gain insight into their chemical composition, morphology, phases, and crystallinity, respectively. In the next step, gas sensors were fabricated using a top electrode (Au/Ti) configuration. Preliminary H$_2$S-gas-sensing studies revealed that GDC gas sensor had a superior gas response to H$_2$S gas than the pristine CeO$_2$ gas sensor at 350°C. The responses of the pristine CeO$_2$ gas sensor to 20 ppm H$_2$S gas was 1.542, while the response of the GDC gas sensor to the aforementioned H$_2$S concentration was 3.489. In addition, the GDC sensor exhibited good selectivity to H$_2$S gas among C$_2$H$_5$OH, C$_7$H$_8$ and NH$_3$ gases. Also, we investigated the response of the sensor in up to 60% relative humidity. The enhanced response of the GDC gas sensor to H$_2$S gas was mainly related to the formation of oxygen defects as a result of Gd-doping in CeO$_2$. Also, good selectivity to H$_2$S was related to the sensing temperature, the higher reactivity of H$_2$S relative to other gases and the small bond energy of H-SH. This study demonstrates the promising ability of Gd-doping to enhance the H$_2$S gas-sensing characteristics of CeO$_2$, which can be applied to other similar systems based on semiconducting metal oxides.

Keywords: H$_2$S, CeO$_2$, Gd-doped CeO$_2$ (GDC), gas sensor, sensing mechanism.

1. INTRODUCTION

Hydrogen sulfide (H$_2$S) is a flammable, colorless, toxic, and corrosive gas [1]. It is generated from certain industrial activities and the degradation of domestic human waste [2,3]. In addition, it is generated by the bacterial breakdown of some organic matter in the absence of oxygen [4]. Exposure to low concentrations of H$_2$S gas causes eye irritation and damage to the respiratory and central nervous systems [5], and prolonged exposure to ppb levels of H$_2$S may increase the risk of central nervous and respiratory symptoms [6]. Exposure to high H$_2$S levels (100 ppm) leads to sudden collapse with difficulty breathing, and is fatal in most cases [7]. Hence, the threshold limit value (TLV) for H$_2$S exposure for 8 h was set to 10 ppm [8]. In addition to its detrimental effects, H$_2$S can act as a biomarker. For example, – if the H$_2$S concentration is > 250 ppb in a person’s exhaled breath, it indicates the presence of periodontal disease [9]. Accordingly, the accurate detection of H$_2$S is important from different perspectives.

Electrochemical, optical, piezoelectric, and resistive-based gas sensors are the gas sensors primarily used for H$_2$S gas-sensing [10,11]. Among them, metal oxide gas sensors, whose resistance changes in a H$_2$S gas environment, are
among the most popular because of their high sensitivity, fast response, high stability, simple operation, and low cost. SnO$_2$, ZnO, Fe$_2$O$_3$, and In$_2$O$_3$ are among the most commonly used metal oxides in sensing studies [14].

2 dimensional (2D) materials are also promising candidates for gas sensing studies [15]. They not only have unique electrical properties but also offer a high surface area for incoming gas molecules [16,17]. 2D metal oxides such as ZnO nanoflakes [18], Fe$_2$O$_3$ nanosheets [19], 2D transition metal dichalcogenides such as WS$_2$ [20] and MoS$_2$ [21] and 2D metal sulfides such as SnS$_2$ [22, 23] are increasingly used in this area. As an example, Zhang et al. [24], used different amounts of Ce as a dopant in ZnO porous nanosheets for an aniline sensing application. It was found that a 1 at% Ce-doped ZnO sensor exhibited a high response of 15.1 to 100 ppm aniline at room temperature.

In addition, CuO-based gas sensors are primarily used for H$_2$S gas sensing [25]. However, less attention has been paid to other semiconducting metal oxides, including rare earth oxides such as cerium oxide (CeO$_2$). CeO$_2$ has a high oxygen storage feature thanks to its rich oxygen vacancies and low redox potential, between Ce$^{3+}$ and Ce$^{4+}$. It is currently employed in three-way catalysts in cars to decrease the emission of pollutant gases [27,27]. Gd$^{3+}$-doped CeO$_2$ has good oxygen ion conductivity and hence, is used in solid oxide fuel cells [28]. Moreover, CeO$_2$ with good absorption of ultraviolet (UV) light is used as a UV shielding and blocking material [29].

There are some studies in the literature regarding the gas sensing applications of CeO$_2$. Pt-decorated CeO$_2$ nanowires (NWs) have been used for CO detection [30]. Motaung et al. used CeO$_2$-SnO$_2$ nanocomposites for H$_2$ gas sensing. Ahmad et al. [31] used ZnO-doped CeO$_2$ to detect nitroaniline gas. Abud et al. [32] used Gd-doped (7 wt. %) CeO$_2$ for CO$_2$ gas sensing and found that it had better performance relative to a pristine CeO$_2$ gas sensor. Zakaria et al. [33] used Zr- and V-doped CeO$_2$/TiO$_2$ core-shell gas sensors for ethanol sensing. However, less attention has been paid to the H$_2$S sensing properties of CeO$_2$. Among the limited studies, Li et al. [34] used CeO$_2$ nanowires for H$_2$S sensing at 25°C, and Oosthuizen et al. [35] used CeO$_2$ gas sensors for sensing both NO$_2$ and H$_2$S gases.

In addition, Gd doping can enhance the gas sensing ability of compounds. For example, it has been demonstrated that 4 wt. % Gd-doped ZnO had a better xylene response than undoped ZnO [36]. In another study, a Gd-doped WO$_3$/RGO nanocomposite exhibited high sensitivity and selectivity for acetone [37]. Fareed et al. [38] reported the enhanced oxygen-sensing properties of a Gd-doped Co$_3$O$_4$ gas sensor. Gd-doped WO$_3$ and Gd-doped WO$_3$/TiO$_2$ nanocomposites exhibited an improved response to NH$_3$ gas [39]. In addition, a 3 % Gd-doped SnO$_2$ gas sensor displayed a large sensor response toward ethanol, which was approximately 26 times higher than that of the pristine sensor [40]. The Gd-doped CeO$_2$ (GDC) gas sensor exhibited good acetone sensing performance [41].

Inspired by the lack of studies on the H$_2$S-sensing feature of GDC, we investigated the H$_2$S-sensing characteristics of pristine CeO$_2$ and GDC nanoparticles (NPs). The results demonstrated that the GDC gas sensor had a higher H$_2$S gas-sensing performance than pristine CeO$_2$, implying the promising ability of Gd doping to enhance the H$_2$S gas response.

2. EXPERIMENTAL

2.1 Materials
Commercial CeO$_2$ (99.9%, Daejung Chemicals & Metals Company, LTD) and GDC (Ce$_{0.9}$Gd$_{0.1}$O$_2$, Rhodia, ULSA grade) NPs were used as the sensing materials in this study.

2.2. Materials Characterization
The morphology, chemical composition, phase and chemical states of the synthesized powders were studied by Transmission electron microscopy (TEM; Talos F200X, FEI), energy-dispersive X-ray spectroscopy (EDS; Talos F200X, FEI), X-ray diffraction (XRD, SmartLab, Rigaku) and X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific Co.), respectively.

2.3. Gas Sensor Tests
Initially, a bilayer (Au/Ti) electrode was sputtered on the samples, already on a substrate. The fabricated gas sensors were put inside a temperature-controlled gas chamber in a tubular furnace. The sensing properties of the sensors were evaluated at different temperatures. Highly pure gases in
certificate cylinders were mixed with synthetic air to prepare the target gas with the desired concentration using mass flow controllers (MFCs). The flow rate was fixed at 500 sccm using MFCs. The resistance of the sensor in air ($R_a$) and in the presence of the target gas ($R_g$) was recorded using a Keithley 2400 source meter connected to a PC, and the sensor response was evaluated as $R = R_a/R_g$. The sensing behavior was also measured in humid air (relative humidity (RH) of 0, 30 and 60 %, measured at 25°C). The actual temperature and RH values of the mixed humid gas was measured before loading into the gas chamber by a sensitive RH probe.

3. RESULTS AND DISCUSSION

3.1. Morphological, Structural, and Chemical Studies

Fig. 1(a) shows a typical TEM image of GDC NPs with sizes of approximately 100 nm. Fig. 1(b) presents a high-resolution TEM (HRTEM) image of GDC and shows the good crystallinity of the GDC. Fig. 1(c)–(f) show the TEM-EDS mapping analyses of the GDC NPs. All expected elements, namely Ce (Fig. 1(d)), O (Fig. 1(e)), and Gd (Fig. 1(f)), were present in the analyzed material, with uniform
distribution across the material. Further chemical analyses were performed using TEM-EDS point analysis, as shown in Fig. 1(g)–(i) for the GDC NPs. Chemical analysis of GDC was recorded at two different points, as shown in Fig. 1(h)–(i). Table 1 shows the results of EDS analysis at the indicated points. For point (h), the weight percentages (wt. %) of the Ce, O, and Gd elements were 76.53, 14.84, and 9.53 %, respectively. In addition, for point (i), the values were 71.28, 17.92, and 10.80 %, respectively. Negligible variations were observed between the two points, demonstrating the excellent chemical homogeneity of the GDC NPs used in this study.

Table 1. Chemical composition of points indicated in Fig. 1g.

<table>
<thead>
<tr>
<th>Element</th>
<th>Point h</th>
<th>Point i</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>35.32 (75.63)</td>
<td>29.97 (71.28)</td>
</tr>
<tr>
<td>O</td>
<td>60.72 (14.84)</td>
<td>65.99 (17.92)</td>
</tr>
<tr>
<td>Gd</td>
<td>3.97 (9.53)</td>
<td>4.05 (10.80)</td>
</tr>
</tbody>
</table>

3.2. Gas Sensing Studies

After a series of preliminary measurements, 350°C was found to be the optimal sensing temperature for both gas sensors, and other tests were performed at this temperature. Fig. 3(a) and (b) show the real time resistance plots of the pristine CeO$_2$ and GDC gas sensors, respectively, at 2, 6, 10, and 20 ppm H$_2$S at 350 °C. For both gas sensors, the resistances decreased after H$_2$S gas injection, indicating the n-type nature of both gas sensors, arising from the n-type conductivity of the CeO$_2$ NPs. In addition, the resistance of the GDC gas sensor was significantly lower than that of the pristine CeO$_2$ gas sensor. Fig. 3(c) compares the responses of gas sensors to various concentrations of H$_2$S gas. The responses of the pristine CeO$_2$ gas sensor to 2, 6, 10, and 20 ppm H$_2$S gas were 1.108, 1.255, 1.352, and 1.542, respectively, while those of the GDC gas sensor to the aforementioned H$_2$S concentrations were 1.532, 2.162, 2.618,
and 3.489, respectively. Hence, the GDC gas sensor had a greater response to H$_2$S gas than the pristine CeO$_2$ gas sensor, reflecting the promising effects of Gd doping for H$_2$S gas sensing.

Fig. 4(a)–(c) present the real time response curves of the pristine CeO$_2$ sensor to various concentrations of H$_2$S gas in the presence of 0, 30, and 60 % RH. Dynamic response curves of GDC gas sensor to various concentrations of H$_2$S gas in the presence of (d) 0, (e) 30, and (f) 60% RH. Calibration curves of (g) pristine CeO$_2$, and (h) GDC gas sensors to H$_2$S gas in the presence of various levels of humidity. (i) Enlarged view of indicated part in Fig. 4(h).

Next, we evaluated the selectivity of the GDC gas sensor. To this end, we exposed it to 20 ppm H$_2$S, C$_2$H$_5$OH, C$_7$H$_8$, and NH$_3$ gases at 350 °C, as shown in Fig. 5(a)–(d), respectively. The corresponding selectivity pattern for the GDC gas sensor is given in Fig. 5(e). The responses to 20
ppm \( \text{H}_2\text{S} \), \( \text{C}_2\text{H}_5\text{OH} \), \( \text{C}_7\text{H}_8 \), and \( \text{NH}_3 \) were 3.489, 2.035, 1.446, and 1.279, respectively. Hence, the response to \( \text{H}_2\text{S} \) was more than that of the other gases, and the sensor showed selectivity towards \( \text{H}_2\text{S} \) gas.

### 3.3. Proposed Gas Sensing Mechanism

Initially, in dry and fresh air, oxygen molecules are adsorbed on the surface of the sensing materials, and because of high electron affinity, take the electrons from the conduction band of CeO\(_2\) and thus will be converted to ionic species such as \( \text{O}_2^- \), \( \text{O}^- \), and \( \text{O}_2^{2-} \) as follows [45]:

\[
\text{O}_2(g) \rightarrow \text{O}_2(\text{ads}) \tag{1}
\]

\[
\text{O}_2(\text{ads}) + \text{e}^- \rightarrow \text{O}_2^-(\text{ads}) \tag{2}
\]

\[
\text{O}^-(\text{ads}) + \text{e}^- \rightarrow 2\text{O}^- \tag{3}
\]

\[
\text{O}^- + \text{e}^- \rightarrow \text{O}^{2-} \tag{4}
\]

This results in the formation of an electron depletion layer (EDL) on CeO\(_2\) in air. After exposure to \( \text{H}_2\text{S} \) gas, the following reaction is likely to occur [45,46]:

\[
\text{H}_2\text{S} + 3\text{O}^- \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 3\text{e}^- \tag{5}
\]

\( \text{H}_2\text{S} \) gas reacts with the already adsorbed oxygen ionic species, causing the release of electrons from the surface of the gas sensor. This leads to narrowing of the EDL, which results in a decrease in resistance, contributing to the sensing signal. Moreover, in the contact areas between the CeO\(_2\) NPs, homojunction barriers are formed in air, which can act as barriers to the flow of electrons from one grain to another (Fig. 6(a)). Upon exposure to \( \text{H}_2\text{S} \) gas, the released electrons are transferred back to the sensor. This results in a decrease in the height of the homojunction barriers in the \( \text{H}_2\text{S} \) gas atmosphere, contributing to the sensing signal (Fig. 6(b)).

A higher response was observed with the GDC sensor. In addition to the abovementioned mechanisms, namely the modulation of the EDL and homojunction barriers, other factors should be considered. As shown by the characterization studies, the GDC gas sensors had approximately 10 wt. % \( \text{Gd}^{3+} \) in its composition. The addition of \( \text{Gd}^{3+} \) to CeO\(_2\) can generate oxygen vacancy defects, which can affect the sensing properties of the GDC. \( \text{Gd}^{3+} \) doping of CeO\(_2\) can introduce vacancies in the oxygen sub-lattice as charge-compensating defects [47]:

\[
\text{Gd}_2\text{O}_3 \xrightarrow{2\text{Gd}^{3+}} 2\text{Gd}_{\text{Ce}}^0 + 3\text{O}_{\text{v}} + \text{V}_{\text{O}} \tag{6}
\]

Thus, oxygen vacancies play a role as favourable adsorption sites for oxygen molecules, and hence, more oxygen will be adsorbed on the surface of the gas sensor and eventually more reactions with \( \text{H}_2\text{S} \) can lead to a higher
sensitivity GDC gas sensor. The selectivity to H$_2$S gas can be attributed to the sensing temperature, a higher reactivity of H$_2$S relative to other gases and the small bond energy of H-SH. The bond energy of H-SH in H$_2$S is 381 kJ/mol, while the bond energy of H-NH$_2$ in NH$_3$ is 435 kJ/mol, and the bond energy of H-OC$_2$H$_5$ in C$_2$H$_5$OH is 635 kJ/mol; thus, H-SH can be easily broken to react with the absorbed oxygen ions [46].

4. CONCLUSIONS

This study analyzed the H$_2$S gas-sensing characteristics of pristine CeO$_2$ and GDC NPs. Different techniques were used to characterize the powders and to gain insights into their morphologies, chemical compositions, and phases. The H$_2$S gas-sensing studies revealed that the GDC gas sensor had a higher response to H$_2$S gas than pristine CeO$_2$ NPs, demonstrating the promising effects of Gd doping on the H$_2$S gas-sensing properties of CeO$_2$ NPs. Moreover, the GDC sensor exhibited a higher selectivity to H$_2$S gas than other interfering gases, such as ethanol, ammonia, and toluene, reflecting its selectivity to H$_2$S gas. The enhanced response of the GDC gas sensor was related to the generation of oxygen defects as a result of Gd doping. Future studies should focus on noble metal decoration to further enhance the gas sensing properties of the GDC.

AUTHORS’ CONTRIBUTIONS

Changhyun Jin and Sangwoo Kim had equal contribution as co-first authors. All the authors discussed the results and commented on the manuscript.

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