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Development of gas sensor based on fractal substrate structures

Anyan Jiang, Fengchun Tian, Member, IEEE, James Anthony Covington, Member, IEEE, Maogang Jiang and Zhiyuan Wu

Abstract—Gas sensor plays a key role in many applications with sensitivity being a critical performance characteristic. Increasing the surface area of gas sensing material is one approach that can increase sensitivity. Fractal geometries, which have large specific surface area and special fractal dimension, have previously been successfully used in the design of macro and microstructures of gas sensors to improve their performance. In this paper, the influence of geometrical structure of the substrate on the gas sensor performance has been investigated. Two fractal structures (Koch snowflake and Menger sponge) and one traditional structure (Cylinder) were fabricated by 3D printing and coated in Ag: MWCNTs based sensing materials. The fabricated sensors were tested with nitrogen dioxide at different temperatures and humidity. Experimental results show that the sensitivity of gas sensors with fractal structures is increased more than twice that of those with traditional geometrical structures.

Index Terms—Gas sensor, Fractal geometry, Specific surface area, Sensitivity, 3D printing technology.

I. INTRODUCTION

Gas sensors have been widely used in many fields, including environmental monitoring [1], food safety [2] and medical diagnostics [3]. Commonly used gas sensors are based on semiconducting [4], electrochemical [5] and biosensing principles [6]. However, the sensitivity and/or LoD (Limit of Detection) of many kinds of gas sensors is not sufficient for some applications, requiring more sophisticated analytical techniques to be used [7, 8]. Many different approaches have been investigated to improve the sensor’s LoD. Depending on the sensing mechanism, it could include changing the microstructure of gas sensing film (e.g. grain size) [9] or adding dopants or impurities [10]. However, the search for new ways to improve the sensitivity/LoD remains an ongoing focus of gas sensor research.

Previously, special structures, such as core/shell nanostructures [11, 12] and hollow nanoflowers [13], have been developed to improve the performance/sensitivity of gas sensors. A more recent approach is to use fractal geometry [28]. A remarkable feature of fractal geometry is its self-similarity, i.e., the local shape/structure of a system is similar to its global shape/structure [14, 15]. This similarity makes the surface area of fractal bodies much greater than that of traditional Euclidean shapes. Therefore, fractal theory provides an opportunity to develop new gas sensor structures, which in turn, could improve sensitivity [16].

Most previous work has focused on creating sensing films with fractal features. For example, V. A. Moshnikov et al. [17, 18] enhanced the sensitivity of a metal oxide sensing film by the formation of gas sensing layers with percolation cluster fractal structure near the percolation threshold. N. K. Plugotarenko et al. [19] investigated the gas sensing performance of SiO2–SnO2–CuO nanofilms with different fractal structures, which indicated that the maximal gas sensitivity is obtained at the transition of one type fractal structure to another. Zelio Fusco et al. [20] enhanced the performance of their gas sensors by integrating tailored dielectric fractals of TiO2 nanoparticles on Au nanodisk surfaces.

Different fractal structures have different effects on sensing films. Films with porous [21, 22] and core/shell [23, 24] fractal structures have a larger fractal dimension and specific surface area, which can result in higher sensitivity. For films with dendrite-like nanocrystals, a smaller fractal dimension corresponds to finer branches and smaller breakdown voltages, which results in a higher sensitivity [25]. For films with relief fractal structures, a lower fractal dimension corresponds to higher crystallinity, which again results in a higher sensitivity [26, 27].

The application of fractal structures to the substrate of a gas sensor is also a potential way to improve its sensitivity. Traditional gas sensor substrates are mainly of cylindrical or planar geometries, which do not have large specific surface areas, such as the sensors made by Figaro (Japan). Fig. 1 (a) illustrates the structure of a typical semiconductor gas sensor with micro-heating plate, while Fig. 1 (b) shows a zoom-in photo and illustration of a typical semiconductor gas sensor.

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with a cylindrical substrate.

For planar sensors, the authors have previously used electrodes formed from fractal structures to enhance gas sensor performance [28]. In this paper, we report on the design of a new gas sensor substrate based on fractal geometry and compare it with traditional cylindrical geometries. 3D printing was used to fabricate the sensor substrates with different geometries. Ag doped multi-walled carbon nanotubes (Ag:MWCNTs) was synthesized as the sensing material to validate our concept, and nitrogen dioxide was selected as the test gas to verify the effectiveness of our sensor substrates.

![Sensor structure](image)

**Fig. 1.** Structure of a typical semiconductor gas sensor with micro-heating plate (a) and the zoom-in photo of a typical semiconductor gas sensor with a cylinder structure (Pin 1, 3, 4 and 6 are sensing signal electrodes, pin 2 and 5 are heating electrodes) (b).

II. FRACTAL GEOMETRY

A. Fractal Structure

There are many geometrical cubes with fractal structures, which have a wide range of characteristics. For example, the Koch snowflake has an infinite perimeter in a limited area, and the Menger sponge is a universal space curve, i.e., any curve is also a homeomorphic subset of itself. Menger sponge is also a bounded, closed set with zero Lebesgue measure, and its Hausdorff dimension is ln20/ln3. Among all the characteristics, the most useful feature of these structures is the large surface area under limited volume (or the large surface area to volume ratio). In most cases, the gas sensing material is coated on the surface of sensor substrate, and so the large surface area to volume will increase the contacting area between the sensing film and the target gas, which could potentially lead to a gas sensor with high sensitivity.

Researchers have studied the area to volume ratio of several fractal geometries [16]. The surface area to volume ratio for Koch snowflake cube, Koch pyramid, Koch tetrahedron, Sierpinski tetrahedron, Menger sponge, and Cylinder in the $k$-th iteration are shown in Fig. 2. It indicates that the fractal geometries have larger structural area than that of traditional Euclidean ones (e.g., cylinder and sphere), and that the Menger sponge has the largest surface area to volume ratio. In addition, the greater the number of iterations, the higher the surface area to volume ratio. The Koch snowflake cube and Menger sponge were used in this work and are shown in Fig. 3 with different iterations.

![Fractal geometries](image)

**Fig. 2.** Ratio of surface area to volume of the seven typical cubes.

![Fractal construction](image)

**Fig. 3.** Construction processes of Koch snowflake cube (a) and Menger sponge (b) ($k$ is the number of iterations).

Assuming the initial side length of Menger sponge and Koch snowflake cube, and the number of iteration of fractal structure are $a$, $a_1$ and $k$, respectively. The surface areas of these fractal structures can be defined as:

$$S_{\text{Menger}} = S_{\text{Koch snowflake}} = \frac{a^2}{2^{k/2}}$$

$$S_{\text{Bottom of Koch snowflake}} = S_{\text{Koch snowflake}} = \frac{\sqrt{5}}{4} a^2$$

$$S_{\text{Lateral of Koch snowflake}} = L_{\text{Perimeter of Koch snowflake}} = 3 \times 4^k \times \frac{a h}{3^k}$$

B. Sensor Substrate made by 3D Printing

In our experiment, three kinds of sensor substrates (Koch snowflake cube and Menger sponge, as stated earlier, and a cylinder for reference) were designed. The ‘iteration times’ of Koch snowflake cube and Menger sponge were set as $k=4$ and $k=3$, respectively, and the initial side lengths were set as 19.6 mm and 16.2 mm, respectively. The outer radius of Cylinder
was 9.1 mm. The height of these geometries was set at 16.2 mm. The Menger sponge, Koch snowflake cube and Cylinder substrates were designed by 3D modeling software and shown in Fig 4(a). The sensor substrates were fabricated by 3D printing using a nylon filament (P396, EOS, Germany), which has an accuracy/repeatability of 0.1 mm. Only those substrates with group deviation less than 5% were chosen. Fig (b) shows a photo of these fabricated substrates.

Fig. 4. Models of Menger sponge, Koch snowflake cube and Cylinder (a) and a photo of 3D printed substrates.

Generally, the volume is equal to bottom area times height. The volume of Koch snowflake cube, Menger sponge and Cylinder can be calculated as:

\[ V = \frac{4}{3} \pi a^3 \times h = \frac{a^2}{12} \times (1 + \frac{4}{9} + \frac{4}{9}) h = 4249.471 \text{mm}^3 \]  \hspace{1cm} (2)

where \( a = 16.2 \text{ mm}, a_1 = 19.6 \text{ mm} \) and \( h = 16.2 \text{ mm} \).

The surface area to volume ratio of Menger sponge, Koch snowflake cube and Cylinder are given in Eq. (3), which indicate that the Menger sponge has the largest surface area.

\[ \frac{S}{V} = 2 \frac{2S_{\text{Koch snowcube}} + S_{\text{Lateral area}} + S_{\text{Inner cylindrical surface}}}{V_{\text{Koch}}} = \frac{2\sqrt{3} a_1^2 + \sqrt{3} a_1^2 - (1 + \frac{4}{9} + \frac{4}{9}) - \pi r^2}{3} + \frac{4^4 a_1^2 h - 2\pi rh}{3} \]

\[ = 0.919 \text{mm}^2/\text{mm}^3 \]  \hspace{1cm} (3)

III. EXPERIMENT

A. Chemicals

Silver nitrate (AgNO_3) and Sodium citrate (C_6H_5Na_3O_7·2H_2O) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All reagents used are of analytic purity and required no further purification. Deionized water was used in all synthesis and fabrication processes. Carbon nanotube dispersion were purchased from Chinese Academy of Sciences Chengdu Organic Chemistry Co., Ltd. and its main characteristics are shown in Table I.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>MWCNTs</th>
<th>Characterization method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer Diameter</td>
<td>nm</td>
<td>8-15</td>
<td>HRTEM, Raman</td>
</tr>
<tr>
<td>Purity</td>
<td>wt%</td>
<td>&gt;95</td>
<td>TGA &amp; TEM</td>
</tr>
<tr>
<td>Length</td>
<td>μm</td>
<td>~50</td>
<td>TEM</td>
</tr>
<tr>
<td>Special Surface Area</td>
<td>m²/g</td>
<td>&gt;140</td>
<td>BET</td>
</tr>
<tr>
<td>ASH</td>
<td>wt%</td>
<td>&lt;1.5</td>
<td>TGA</td>
</tr>
</tbody>
</table>

B. Synthesis of Ag:MWcnts Samples

The classical Lee method was used to prepare the Ag sol [29]. The preparation process of Ag:MWcnts is shown in Fig 5(a). In detail, 270 mL multi-walled carbon nanotubes (MWCNTs) dispersion with a concentration of 0.5 mg/mL was obtained and ultrasonic dispersed in a beaker for 10 minutes. Then 36 mg AgNO_3 and 60 mg C_6H_5Na_3O_7·2H_2O were added to the beaker. The as-obtained solutions were magnetically stirred at 95°C for 45 minutes, and then cooled naturally down to room temperature with continuous magnetic stirring. The resulting products were separated from the reaction medium by centrifuging at 15200 r/min for 1 hour and rinsed with deionized water. The centrifugation process was repeated twice, then 30 mL of deionized water was added for dilution, and ultrasonic dispersion was carried out for 15 minutes.

C. Fabrication and Characterization of gas sensors

Before gas testing, a pair of electrodes and wires were placed on each end of the 3D substrates. The electrodes and wires were then coated and connected by conductive silver paste (LUXIANZI, China). The Ag:MWcnts solution and the 3D sensor substrates were transferred to a 100 mL Teflon-lined stainless steel autoclave, heated at 95°C for 6 hours. Once the autoclave had cooled down to room temperature, the sensors were rinsed with deionized water and dried in an oven at 60°C for 30 minutes. The fabrication process is shown in Fig 5(b). The morphological character and microstructure of as-prepared films were characterized by field emission scanning electron microscopy (FESEM, FEI Nova400) with an acceleration voltage of 20 kV, and an energy dispersive X-ray spectroscopy attached to the SEM.
Fig. 5. Preparation of Ag:MWCNTs (a) and fabrication process of sensors (b).

D. Measurement of Sensor Performance

Fig. 6 shows the setup used for sensor testing and the schematic diagram of the test circuit. In total, 15 sensors were used (5 of each type). Inside the test chamber (Teflon coated) a temperature & humidity sensor (SHT15, SENSIRION, Switzerland) was placed. The chamber was put into an electric drying oven (DHG-9053A, SuoKe, China), which was used to control the ambient temperature. A programmable linear DC power supply (SPD3303C, SIGLEVT, China) was used to provide a working voltage for the sensors and the output voltage was measured by a data acquisition card (USB3000, Art Technology, China), with the resultant data transferred and stored on a computer. To avoid oxidation of Ag by O₂, we only used N₂ as the carrier gas, as this study focuses on the sensor substrates. The sensors were first exposed to dry N₂ for 10 minutes, followed by injection of the target gas (NO₂) for a further 10 minutes, then the oven was heated to 70 °C for 10 minutes to accelerate the sensor desorption and then cooled down to the experimental temperature, till the sensor returned to its baseline resistance. In these experiments, NO₂ was used at five different concentrations (0.25, 3, 6, 9, 12 ppm). The sensor response to NO₂ was defined here as \( S = \frac{R_a - R_g}{R_a} \), where \( R_a \) and \( R_g \) is the resistance of the sensing layer measured in N₂ and NO₂, respectively. Sensitivity is defined as the slope of the linear fitting equation of the response curve.

IV. RESULTS AND DISCUSSION

The SEM and elemental mapping images of the Ag:MWCNT film are shown in Fig 7. Fig 7(a) shows that the arrangement of MWCNTs is disordered and intertwined. The Ag nanoparticles, which are of spherical shape, are effectively modified on the outer wall of MWCNTs. Fig 7(b) shows that many Ag nanoparticles are adsorbed on the surface of MWCNTs. Although there are aggregations of Ag nanoparticles in some places, the overall distribution is relatively uniform. Fig. 8 shows the dynamic response of one of the Menger sponge upon exposure to NO₂ (0.25, 3, 6, 9 and 12 ppm) at 25 °C & 10% RH, which exhibits a NO₂ concentration dependent response. The sensor resistance gradually returns to its initial level, after the gas was removed. To speed up this process a heating cycle was also performed before the sensors were returned to the experimental temperature [30].

Fig. 7. SEM image (a) and Elemental mapping images (b) of the Ag:MWCNTs film.
Fifteen sensors were used (with the three kinds of substrates: Menger sponge, Koch snowflake and Cylinder; Substrate number of each kind is 5) for performance (including repetition) test. Response curves of sensors to NO$_2$ (0.25, 3, 6, 9 and 12 ppm) at 25 °C, 10% RH and corresponding piecewise linear fitting equation of different concentrations are shown in Fig. 9. This shows that the response of the sensors with Menger sponge and Koch snowflake structures are better than those with Cylinder structures. Here, the sensitivity is proportional to the surface area to volume ratio [16]. Theoretically, the surface area to volume ratio of the Menger sponge, Koch snowflake cube and Cylinder are 1.528, 0.919 and 0.439 respectively. This indicates that the sensors with Menger sponge structures and Koch snowflake structures could potentially have 3.48 times and 2.09 times, respectively, greater sensitivity compared to the Cylinder structure. Fig. 9 (b) shows that sensors with Koch snowflake structures have around 2.18 times the sensitivity compared to the Cylinder structure, at 3~12ppm NO$_2$. However, the sensors with Menger sponge structures are no better than those with Koch snowflake structures, with an increase in sensitivity of around 2.05 compared to the Cylinder structure. Potential reasons for this, maybe a limitation of the 3D printer, which cannot fully fabricate the internal pore structure. Also, the inner pore structure of the Menger sponge may increase the time taken for the target gas to contact the sensing material, and thus the sensors may not have fully responded by the end of the experimental period. In the future, we will use a micron level printing approaches and update our gas testing system to reduce the time taken for the target gas to arrive at the internal gas sensing surfaces. In addition, this micron level printing may allow us to attain even higher surface area to volume ratios, which theoretically may be 10$^7$ greater than that of Cylinder (Fig. 2). It can be speculated that much higher sensitivity can be obtained with these substrate structures.

Gas sensor responses using carbon nanotubes can be affected by temperature and humidity [30]. Thus, experiments were repeated at 40 and 55°C at 10% RH, with the corresponding results are shown in Fig. 10. The process of gas humidification is described in Fig. S1, Supporting Information. The resistance of the sensors decreased as the temperature increased (Fig. S2, Supporting Information). The responses increased at 40°C and decreased further at 55°C. This is likely due to the change of adsorption and desorption rate with temperature. There was only one sensor (outlier), with a Cylinder structure that had a higher response than some other sensors with fractal structures (Fig. S3, Supporting Information). Fig. 10 shows that the averaged response of the sensors with Cylinder structure are lower than those with fractal structures.

The sensing tests of NO$_2$ (0.25, 3, 6, 9 and 12 ppm) at 30°C, 20% RH, 50% RH and 80% RH were also conducted, and the corresponding results are shown in Fig. 11. The sensor resistance and response increased as the humidity level was raised (Fig. S4, Supporting Information). The reason behind this is associated with the adsorption of water molecules. For MWCNTs, the main absorption route is physical and the...
accumulation pores and outer surface of the accumulation, formed by intertwining of MWCNTs, are the main adsorption centers. The adsorption of water molecules weakens the van der Waals force between MWCNTs, which increases the gaps among MWCNTs. This in turn increases the porosity and enhances the adsorption performance. The results indicate that sensors with fractal structures have a higher response than those with a Cylinder structure, except one outlier (Fig. S5, Supporting Information). As can be seen in Fig. 11, the response and sensitivity of sensors with fractal structures are greater than those of Cylinder under different humidity conditions.

![Graph showing response curves of sensors to NO\textsubscript{2} at different RH](image)

**Fig. 11.** Averaged response curves of sensors to NO\textsubscript{2} at 20% RH, 50% RH and 80% RH at 30°C.

Fig. 12 shows the stability of one of the Menger sponge sensors at 25°C, 10% RH in N\textsubscript{2} and 300 ppm NO\textsubscript{2}. The measurements were conducted for 7 days and the resistances in N\textsubscript{2} and 300 ppm NO\textsubscript{2} were recorded at daily intervals. In Fig. 12, the baseline resistance changes between 3373 Ω and 3377 Ω, while the response resistance varies between 2959 Ω and 2982 Ω. It shows that the maximum deviation of the baseline and response resistances is less than 5% from the initial value, reflecting an excellent stability over the test period (Fig. S6, Supporting Information).

![Graph showing week stability tests of sensors to NO\textsubscript{2}](image)

**Fig. 12.** Week stability tests of sensors to 300 ppm NO\textsubscript{2} at 25°C, 10% RH: the dynamics response curve of one of the Menger sponge sensors to 300 ppm NO\textsubscript{2} (a) and the corresponding baseline resistance $R_0$ and response resistance $R_\text{g}$ (b).

This work has shown that using fractal substrate geometries does lead to an increase in response over traditional substrates, at the same scale. A limitation of this study is the dimensions of the substrates generated. However, using micron or even smaller level 3D printing with high accuracy (or similar manufacturing techniques) will produce much smaller substrates and potentially, result in much higher sensitivity and reproducibility. Another limitation of our study is that the structures were fabricated with nylon. It inhibits the use of materials with higher operating temperatures, such as metal-oxides. In our following work, we will investigate the use of 3D printing of ceramic structures to remove this limitation, including the integration of metal heater and electrode structures.

**V. CONCLUSION**

In this paper, the influence of substrate structure on gas sensor sensitivity was studied. Fractal theory was applied to the structural design of the gas sensor substrate. Sensors with Menger sponge, Koch snowflake and Cylinder substrate structures were fabricated by 3D printing and NO\textsubscript{2} was used as the target gas to test their performance. Experimental results show that the sensors with fractal structures have a greater response and sensitivity than those sensors with a Cylinder structure. Our next steps will be to develop ceramic based fractal structures allowing much higher operating temperatures or selecting better gas sensing materials, such as metal oxide semiconductor [31] or polymer etc. [32].

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