CRUMPLED AND STRETCHABLE GRAPHENE GAS SENSOR WITH ENHANCED SENSITIVITY TO HYDROGEN

Zhichun Shao¹, Takeshi Hayasaka¹, Huiliang Liu², Jiaming Liang², Yichuan Wu² and Liwei Lin¹,²

¹Berkeley Sensor and Actuator Center, University of California Berkeley, USA
²Tsinghua-Berkeley Shenzhen Institute, Shenzhen, China

ABSTRACT

We have successfully demonstrated a stretchable gas sensor with enhanced sensitivity to hydrogen based on crumpled graphene structures. Compared with the state-of-art technologies, three distinctive advancements have been achieved: (1) enhanced sensitivity to hydrogen based on the crumpled graphene at room temperature; (2) a model on the enhanced sensing mechanism on the crumpled graphene surface; and (3) stretchable gas sensor utilizing crumpled graphene with up to 200% stretchability. As such, the proposed sensing scheme and results could open up a new class of graphene-based, stretchable gas sensing systems for environmental and biological monitoring.

INTRODUCTION

Detection of hydrogen gas in the environment is of great importance as hydrogen is generally colorless, odorless, tasteless and highly explosive. There is a continued need for faster, more selective and more accurate detection of hydrogen gas in the industry including hydrogen fuel cell [1], coal mining [2], nuclear safety, metallurgical engineering [3], disease indicator [4] and environmental pollution detection. Traditional hydrogen detection methods, such as gas chromatography and mass spectrometry, are relatively expensive, bulky and slow in terms of response time. In this regard, various kinds of gas sensors based on micro electro-mechanical systems (MEMS) including metal oxide and graphene-based gas sensors [5, 6] have been widely explored. For metal oxide gas sensors, some noble elements such as palladium and platinum are widely used in hydrogen detection. However, these metals are susceptible to volume changes when exposed to hydrogen, leading to cracking, blistering and delamination of metal films [3]. Moreover, metal oxide gas sensors require to operate at relatively high temperature (usually over 200°C) [7], which leads to high power consumption and complex fabrication processes. On the other hand, since the discovery of graphene [8], it has been hoped that graphene-based gas sensors would significantly overcome the shortcomings of the existing gas sensors, because of its excellent properties such as large surface to volume ratio, high mobility, low power consumption, low electrical noise and room temperature operation. However, due to the lack of active sites, few molecules can be adsorbed on the bare flat graphene surface [9, 10], resulting in low sensitivity to target gases such as hydrogen.

Here, we demonstrated a stretchable hydrogen gas sensor with enhanced sensitivity and high stretchability based on crumpled graphene. The crumpled graphene, which is intentionally deformed to have a continuously wavy 3D surface, is fabricated by inducing elastic buckling of graphene during the graphene transfer process [11].

Figure 1a illustrates the undulating graphene surface and the adsorption of gas molecules on the graphene. The white and red gas molecules represent adsorbed hydrogen and oxygen molecules, respectively. A pre-strained elastomer substrate as much as 200% in the prototype tests under the tensile strain condition is used to generate compressive strains on the originally strain-free graphene, surpassing the possible maximum tensile strain of ~25% of flat graphene. Figure 1b shows a fabricated crumpled graphene gas sensor on the elastomer substrate with 200% pre-strain.

More importantly, the sensitivity to hydrogen is greatly enhanced at room temperature due to the introducing of large curvature of crumpled graphene, which distorts the π bonds of graphene and creates a stronger interaction with gas molecules. Differing from the weak charge transfer between hydrogen molecules and flat graphene, hydrogen reacts with the oxygen ions which are strongly adsorbed on the crumpled graphene surface due to the distorted π bonds and releases electrons to the graphene.

Figure 1: a) An illustration of gas adsorption on the undulating graphene surface; b) A fabricated crumpled graphene gas sensor on a stretchable substrate.
Figure 2 explains the enhanced hydrogen sensing mechanism. Figures 2a-b illustrate the weak charge transfer between hydrogen molecules and flat graphene and the corresponding electronic band structure of the graphene sheet. When hydrogen molecules are adsorbed on the flat graphene, a small number of electrons are transferred from graphene to hydrogen molecules, which increases the carrier hole density in the p-type graphene, leading to a slightly decrease of the graphene resistance. Figure 2c illustrates the reaction between hydrogen molecules and oxygen ions adsorbed on the crumpled graphene surface. During the reaction, electrons are released to the graphene sheet, which largely decreases the carrier hole density in the graphene and leads to resistance increase as shown in Figure 2d. Furthermore, the crumple density, height and pitch are modulated by the applied pre-strain, opening up a new class of strain-tunable hydrogen gas sensor. According to the Langmuir model [12], the sensitivity enhancement can be further increased by applying higher pre-strain.

FABRICATION

Chemical-vapor-deposition (CVD)-grown monolayer graphene is used as the sensing material of our device, which is available from Graphenea Inc. Figure 3 illustrates the 6-step process flow to fabricate the crumpled graphene gas sensor. The flat monolayer graphene is transferred onto a biaxially pre-stretched elastomer substrate. For the elastomer substrate, Ecoflex (Ecoflex™ 00-30) polymer substrate is used. The maximum biaxial tensile pre-strain in our prototype devices is about 200% in both $x$ and $y$ directions. After the transfer, the graphene channel can be patterned by an oxygen plasma etching process (50W, 7s). After the graphene channel fabrication, the Au/Pd (30nm/25nm) electrodes are deposited and patterned as source and drain electrodes by e-beam evaporation using shadow mask lithography. The crumpled graphene channel as well as source/drain electrodes are formed after releasing the biaxial pre-strain. The fabrication process of the flat graphene gas sensor on SiO$_2$ and the detailed measurement setup have been reported in our previous work [13, 14].

RESULTS

Figure 4a shows an optical microscopic image of a crumpled graphene channel with source and drain electrodes deposited. Because of the crumples, the graphene channel is not as transparent as the flat graphene. The mechanical performance of the stretchable crumpled graphene gas sensor is demonstrated in Figures 4b-d, with sequentially stretching with about 100% uniaxial strain and twisting. Figure 5 displays the scanning electron microscope (SEM) images of graphene crumples under biaxial pre-strain and uniaxial pre-strain. The biaxial pre-strain is about 200% in both $x$ and $y$ direction and the uniaxial pre-strain is about 100%. The SEM images show that the crumple wavelength $\lambda_c$ is approximately 1-2 $\mu$m.
which is larger than the theoretical estimation [11, 15-17] of:

\[ \lambda = 2\pi h \left( \frac{E_s}{3E_g} \right)^{\frac{1}{3}} \approx 0.33 \mu m \]  

[16]

where \( E = E / (1 - \nu^2) \), \( E \), and \( \nu \) are the plane-strain elastic modulus, Young’s modulus, and Poisson’s ratio of the graphene \((g)\) and substrate \((s)\), respectively, and \( h \) denotes the graphene thickness. This resulting larger wavelength may be due to the increased film thickness from multiple crumpled graphene layers of the CVD-grown graphene.

To investigate the gas sensing capability of crumpled graphene devices, we tested the response under hydrogen of the crumpled graphene devices with varying biaxial pre-strain ranging from 100% to 200% and compare these results with that of flat graphene on SiO₂. Figure 7a shows the dynamic hydrogen sensing results of crumpled and flat graphene at room temperature with hydrogen concentrations from 0.02% (200 ppm) to 0.1% (1000 ppm). The carrier gas is dry air and the gas purging cycle time is 3 minutes.

One can observe that for flat graphene, the resistance drops when exposed to hydrogen, while the resistance increases for crumpled graphene, which is in good accordance with our proposed sensing mechanism. Figure 7b displays the hydrogen sensitivity for both crumpled and flat graphene. From the experimental results, the sensitivity to hydrogen of crumpled graphene with 200% pre-strain is enhanced by 320% than that of the flat graphene and 580% than that of crumpled graphene with 100% pre-strain. The overall electrical and mechanical performance of our crumpled and flat graphene gas sensors are summarized in Table 1.

---

**Figure 5:** SEM images of crumpled graphene under a) 200% biaxial pre-strain and b) 100% uniaxial pre-strain.

**Figure 6:** a) I-V curves and b) sheet resistances for flat and crumpled graphene gas sensors.

**Figure 7:** a) Dynamic hydrogen sensing response curves and b) sensitivity values of crumpled graphene with different pre-strains (100% to 200%) and flat graphene on silicon dioxide at room temperature for hydrogen concentrations from 0.02% (200 ppm) to 0.1% (1000 ppm).
**CONCLUSIONS**

We have successfully demonstrated that engineering the crumples of the graphene film can enhance the sensitivity to hydrogen gas at room temperature. The crumpled graphene gas sensor exhibits a 320% sensitivity enhancement as compared with a flat graphene gas sensor on SiO$_2$. Moreover, we also proposed a model on the enhanced sensing mechanism on the crumpled graphene surface, which shows good accordance with our experimental results. Furthermore, our stretchable gas sensor utilizing crumpled graphene can realize up to 200% stretchability, highly surpassing the possible maximum tensile strain of ~25% of flat graphene and ~1% of SiO$_2$. As such, the proposed sensing scheme and results could potentially open up a new class of graphene-based, stretchable gas sensing systems for environmental and biological monitoring.

**ACKNOWLEDGEMENT**

This work was supported in part by BSAC (Berkeley Sensor and Actuator Center, an NSF/Industry/University collaboration center). These devices were fabricated at the UC Berkeley Marvell Nanofabrication Lab. Professor Liwei Lin is a core-principal investigator of the Tsinghua-Berkeley Shenzhen Institute (TBSI) and we acknowledge the funding support of TBSI.

**REFERENCES**


**CONTACT**

*Z. Shao, tel: +1-510-220-0974; zhichun_shao@berkeley.edu

---

**Table 1: Performance summary of crumpled and flat graphene gas sensors.**

<table>
<thead>
<tr>
<th></th>
<th>Pre-strain 200%</th>
<th>Pre-strain 150%</th>
<th>Pre-strain 100%</th>
<th>Flat graphene on SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity AR/Re under 0.1% H$_2$ (%)</td>
<td>0.58</td>
<td>0.22</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>Maximum stretchability</td>
<td>200%</td>
<td>150%</td>
<td>100%</td>
<td>~1% [18]</td>
</tr>
<tr>
<td>Sheet resistance (kΩ/sq)</td>
<td>6.08</td>
<td>4.85</td>
<td>3.97</td>
<td>0.43</td>
</tr>
</tbody>
</table>