Low temperature hydrogen sensing using reduced graphene oxide and tin oxide nanoflowers based hybrid structure

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Abstract
In this paper, we have demonstrated a low temperature hydrogen (H\textsubscript{2}) sensor based on reduced graphene oxide (rGO) and tin oxide nanoflowers (SnO\textsubscript{2} NFs) hybrid composite film. The addition of SnO\textsubscript{2} NFs into rGO solution inhibits irreversible restacking and agglomeration of rGO and increases the active surface area for interaction with H\textsubscript{2}. This rGO-SnO\textsubscript{2} NFs hybrid film sensor showed an excellent response to H\textsubscript{2} at 60 °C at 200 ppm with an improvement of 126% compared to pure rGO which was used as a control sample. The sensor also showed good response and recovery time in comparison to pure rGO film. The highly improved H\textsubscript{2} sensing characteristics of rGO-SnO\textsubscript{2} NFs hybrid are due to its (a) unique structural geometry that increased the surface area for H\textsubscript{2} adsorption, and (b) change in the width of depletion layer at the interface due to H\textsubscript{2} interaction.

Keywords: reduced graphene oxide, tin oxide, nanorods, composite, sensors

1. Introduction

Hydrogen (H\textsubscript{2}) is considered to be one of the most promising sources of energy for next generation power and transportation sectors [1, 2]. It can be produced from zero-carbon methods such as wind, solar, nuclear power, and fossil sources using complete carbon capture and storage. Its extraordinary properties such as low molecular weight, high energy content and its combustibility without emitting any harmful gases make it an ideal choice for an alternative energy source [2–4]. However, H\textsubscript{2} is very volatile and extremely flammable in nature, therefore a small leak in the atmosphere can cause a potential explosion [1, 5]. Since H\textsubscript{2} is a colorless and odorless gas, it cannot be detected by ordinary human senses [6]. Thus, development of cost effective H\textsubscript{2} sensors with high sensitivity and short response time is essential for safely harnessing energy from hydrogen.

One of the most promising candidates for sensing H\textsubscript{2} is reduced graphene oxide (rGO) which is chemically very facile to synthesize. rGO is a derivative of graphene and widely studied for gas sensing applications due to its high specific area (2630 m\textsuperscript{2} g\textsuperscript{-1}) and high sensitivity [7]. In the recent past, though many studies have been carried out on rGO based H\textsubscript{2} sensing devices, most of those devices resulted in a relatively high working temperature, poor sensitivity, high response and recovery time which are not suitable for practical applications [8, 9].

Metal oxides such as ZnO, CuO, WO\textsubscript{3}, and SnO\textsubscript{2} were also widely investigated for their potential in monitoring various explosive and pollutant gases owing to their unique physical and chemical properties [10–12]. Among these, SnO\textsubscript{2} has attracted much attention in H\textsubscript{2} sensing applications owing to their high chemical stability, low cost, high sensitivity, fast response and recovery time. The sensing
characteristics of SnO₂ are greatly dependent on various parameters such as morphology, porosity, surface-to-volume ratio, and shape [13]. So far, many of the H₂ sensing studies have been carried out on various types of SnO₂ nanomaterials, such as nanoparticles, nanorods, nanoflowers, nanograss, and nanospheres [14–16]. Generally, the sensors made up of those SnO₂ nanostructures require high operating temperatures (200 °C–400 °C) leading to higher power consumption [17]. In most of the cases the as-prepared SnO₂ nanostructures are in powder form and the sensing devices are made out of these nanomaterials using binders which generally degrade the sensing characteristics [18].

An effective way to harness and improve the sensing characteristics of SnO₂ nanostructures will be to use rGO as a binder. Up to now, several rGO based composite materials have been synthesized by incorporation of metal/metal oxide nanoparticles for better sensing properties [19]. Although the above-mentioned methods resulted in a better H₂ sensing property, they still suffer from drawbacks such as high cost and a complex and time consuming process, which limit their wide applications [20, 21]. Moreover, the preparation of composite materials is carried out by an in situ process which usually results in the aggregation of rGO or nanoparticles limiting their efficiency [22].

In this work we have integrated hydrothermally prepared 3D tin oxide nanoflowers (SnO₂ NFs) with solution-processed 2D rGO nanosheets and used them to fabricate a highly sensitive H₂ sensor. The hybrid structure was found to possess structural properties (large surface area) of rGO and electrical properties of SnO₂. The hybrid composite nanostructure (rGO-SnO₂ NFs) exhibits highly enhanced sensitivity to hydrogen at low working temperatures compared to pure rGO. The enhancement in the sensitivity to H₂ is due to the larger surface area and the formation of a charge depletion layer at the rGO-SnO₂ NF’s interface.

2. Materials and methods

2.1. Synthesis of graphene oxide

Graphene Oxide (GO) was synthesized by a modified Hummer’s method [23, 24]. Prior to the drop-casting process, the concentration of the as-prepared GO solution was diluted to 25% by the addition of pure DI water. Then it was ultra sonicated for 45 min to reduce the size of the GO flakes and then centrifuged at 15,000 rpm for 5 min in order to remove the thicker flakes. The top portion of the solution was collected in a vial and stored in room temperature for further use. By using this method we were able to prepare GO sheets 1 μm thick and few microns wide. Figure 1(a) shows the atomic force microscopy (AFM) image of the GO thin film.

2.2. Synthesis of tin oxide (SnO₂) nanoflowers

Tin oxide nanoflowers (SnO₂ NFs) were successfully grown by employing a facile and cost effective hydrothermal method. Conventionally anisotropic growth is achieved by using environmentally harmful surfactants such as Cetyltrimethylammonium bromide (CTAB) and Hexamethylenetetramine (HMTA). In this study we have synthesized SnO₂ NFs without using these surfactants by adopting the following recipe. 0.9 g of NaOH was added to 100 ml of a glass beaker containing 40 ml of DI water followed by magnetic stirring for 30 min. Subsequently, 1.05 g of SnCl₄·5H₂O was added to the above solution while keeping it stirred. After 30 min, 40 ml of ethanol was added to the above solution very slowly which resulted in a white translucent solution. This resultant solution was transferred to a teflon-coated stainless steel autoclave and its temperature was maintained controllably in an oil bath at 200 °C ± 1 for 24 h. The light blue color final product was collected and washed with a copious amount of DI water and ethanol to remove any unwanted chloride ion impurities followed by drying in a convection air oven at 60 °C for 12 h [25].

2.3. Fabrication of gas sensing device

The device fabrication consists of two steps. Firstly, the pre-patterned metal (Ti/Au) electrodes with 4 μm gaps were fabricated by a photolithography technique. Figure 1(b) shows the microscopic image of the interdigitated electrodes fabricated on a SiO₂/Si substrate. Secondly, the sensing layer was prepared by directly drop-casting 0.5 μl of solution on metal electrodes containing GO and SnO₂ NFs followed by annealing at 400 °C. The mixture solution is the uniform dispersion of 0.5 ml GO and 1 mg of SnO₂ NFs powder prepared by ultra sonicating it for 30 min. Under same experimental condition a control sample was prepared by directly drop-casting 0.5 μl of 25% GO. Figure 2 shows the schematic diagram of rGO-SnO₂ NFs based hydrogen sensor. For clarity, only the hydroxyl groups in rGO were considered in the schematic representation.

2.4. Hydrogen gas sensing technique

The gas sensing measurements were carried out in a closed chamber equipped with a PID controlled electrical heater (supplementary figure S1). Before starting the sensing measurement the chamber was evacuated to ~1 × 10⁻³ mbar by a rotary pump. To register the sensing signal, high purity H₂ gas (99.99%) was introduced at optimized concentrations by a

Figure 1. (a) AFM image of the GO thin film drop-coated on Si substrate. (b) Microscope image of the as-fabricated Au electrodes.
mass flow controller (MKS, USA) while monitoring the electrical response of the sensor by current–voltage (I–V) measurement system (Keithley 4200 SCS).

3. Results and discussions

From the FE-SEM images it can be clearly seen that the as-prepared hydrothermally grown SnO2 forms a flower-like structure (figures 3(a) and (b)). Each flower-like structure consists of a large number of nanorods with a common base. The average width of the nanorods was found to be ~74 nm and the length to be ~250 nm. Figures 3(c) and (d) show that SnO2 NFs are integrated into rGO in two ways. In the first case, SnO2 NFs protrude out of the rGO layer, allowing the top portion of the nanoflowers to interact with H2. In the second case, SnO2 NFs are completely covered by the rGO sheets, which are free from wrinkles and agglomerations. The chemical reaction for the formation of SnO2 NFs can be given by,

\[
\text{Sn}^{4+} + 6\text{OH} \rightarrow \text{Sn(OH)}_{6}^{3-} \tag{1}
\]

\[
\text{Sn(OH)}_{6}^{3-} \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \tag{2}
\]

From equations (1) and (2), it can be clearly understood that during the hydrothermal reaction an intermediate product is formed and it decomposes into a large number of small SnO2 nuclei and each nuclei further grows into nanoflowers consisting of a large number of nanorods. Since the growth of these SnO2 NFs was carried out in the absence of surfactant the observed rod-like structure can be attributed to the chemical potential of the water/ethanol and the inherent crystalline structure of the SnO2. For the rutile structure, the surface energy of SnO2 for various crystal faces can be sequenced as (110) < (100) < (101) < (001). It is this inherent crystal property, assisted by an ethanol/water system, which promotes the nuclei to grow anisotropically along the (001) direction forming a nanorods structure by favoring the minimum surface energy [26].

The chemical composition of GO, rGO and rGO-SnO2 NFs hybrid structures were investigated by x-ray photoelectron spectroscopy (XPS) analysis. Figure 4(b) shows the survey spectrum of rGO and rGO-SnO2 NFs. The bands observed at 284.6 and 530.4 eV are attributed to carbon (C) and oxygen (O) 1s core level binding energies, respectively [27]. In rGO-SnO2 NFs, apart from C1s and O1s peaks, several bands associated with the Sn element were also observed. The Sn 3d spectrum of rGO-SnO2 NFs (figures 4(b) and (d)) observed at 487.3 eV and 494.9 eV, confirms the presence of SnO2 NFs in the hybrid structure [22, 28]. The C1s spectrum of GO and rGO-SnO2 NFs are given in figures 4(a) and (c) exhibiting three peaks at 284.6, 286.8 and 288.7 eV, attributed to C–C, C–O and C=O bands. The presence of C–O and C=O peaks in the C1s spectrum of rGO-SnO2 NFs implies that oxygen-containing groups such as hydroxyl, carbonyl, and epoxide are still present, even after the annealing treatment [27, 28]. However, the peak intensities of C–O and C=O have tremendously decreased compared to untreated GO (figure 4(d)) suggesting that most of the functional groups in rGO-SnO2 NFs have been removed after annealing at 400 °C.

The as-fabricated sensing devices, both rGO and rGO-SnO2 NFs, were initially tested for room temperature (~25 °C) conductivity by carrying out current–voltage (I–V) measurement. This is done to confirm the presence of rGO, as the parent material GO is non-conductive due to the extensive presence of saturated sp3 bonds, high density of electron-negative oxygen atoms bonded to carbon and other defects. From I–V characteristics (figure 5), the resistance of the rGO based device is found to be ~20 kΩ which indicates that GO has been reduced successfully. The linearity of the I–V curve shows that the contacts have a very low Schottky barrier. After the addition of SnO2 NFs to rGO, the resistance increased to ~30 MΩ, which is three orders of magnitude greater than the pure rGO sample. This can be attributed to
the formation of a depletion layer at the interface between SnO$_2$ NFs and rGO [22].

Figures 6(a) and (b) shows the resistance variation of the control sample and rGO-SnO$_2$ NFs composites upon exposure to H$_2$ measured at room temperature (RT) and 40 °C, respectively. The measurements were performed for different concentrations of H$_2$ ranging from 200–1000 ppm. The time used for introduction (ON) and removal (OFF) of H$_2$ was 400 s and 300 s, respectively. At room temperature, when hydrogen is ‘ON’ the resistance of the device increased resulting in a peak (p-type conductivity) and it decreased to 40 °C resulting in a valley (n-type conductivity). By plotting both the curves together we can clearly see that the peak and valleys occur in the opposite phase. This is an effect commonly seen in chemically processed samples where a significant number of vacancies exist, and defects and hydroxyl group over which oxygen gets weakly adsorbed. On slightly increasing the surface temperature oxygen gets desorbed leaving the sample surface electron rich. A similar kind of behavior was observed in rGO by Le-Sheng Zhang et al [29].

The sensing response, response time and recovery time of both the devices were studied in order to understand the effect of incorporation of SnO$_2$ NFs into rGO nanosheets. The response of the device is defined as [30],

$$\text{Response} = \left( \frac{R - R_o}{R_o} \times 100\% \right)$$  \hspace{1cm} (3)

Where, $R$ is the resistance of the sample exposed to the gas and $R_o$ is the baseline resistance in air. The H$_2$ sensing response of the as-fabricated sensors, both rGO and rGO-SnO$_2$ NFs, was carried out in a gas sensing chamber as described in the experimental section. H$_2$ was introduced (400 s) and removed (300 s) from the chamber periodically. Both introduction and removal of H$_2$ was considered as a single period (700 s). The H$_2$ concentration was varied after each period and the concentrations used were 200, 500, 800

Figure 4. High resolution XPS and curve fit of (a) C 1s in untreated GO, (b) XPS survey spectra of rGO with and without SnO$_2$ NFs. High resolution XPS and curve fit of (c) C 1s in rGO-SnO$_2$ NFs hybrid composite and (d) Sn3d in rGO-SnO$_2$ NFs hybrid composite structure.

Figure 5. I–V characteristics of rGO and rGO-SnO$_2$ NFs hybrid composite annealed at 400 °C.
and 1000 ppm, resulting in a sensing curve containing four periods in series for a particular operating temperature.

Figures 7(a)–(c) show the sensing responses of both rGO and rGO-SnO2 NFs at different operating temperatures. The operating temperatures used for the sensing measurement were 40 °C, 50 °C, and 60 °C. From the room temperature sensing curve (figure 7(b)), it can be clearly seen that the addition of SnO2 NFs into rGO clearly improves the sensing response. The improvement becomes very remarkable when the operating temperature is increased to higher values (40 °C and 60 °C). The responses of rGO-SnO2 NFs at 60 °C were found to be 19.6%, 21.2%, 22.74% and 22.91% for the concentration of 200, 500, 800, and 1000 ppm respectively. For the same concentration and operating temperature, the responses of rGO were calculated to be 8.6%, 9.59%, 10.28% and 10.51% and its highest response for 200 ppm was 22.2% at 150 °C. For e.g. at 60 °C the response of rGO has been improved by 126% for 200 ppm due to the addition of SnO2 NFs. To understand the effect of SnO2 NFs on the sensing response of rGO, the surface microstructure Brunauer–Emmet–Teller (BET) analysis of rGO and rGO-SnO2 NFs samples was carried out and the results were given in the supplementary information. Figure S2 shows the adsorption and desorption isotherms of rGO-SnO2 NFs and rGO. These results clearly indicate that incorporation of SnO2 NFs into rGO increases the effective surface area of the interaction of gas species (H2), resulting in improved sensing characteristics of rGO-SnO2 NFs compared to the pure rGO sample. We have also gathered sensing data from the published literature and listed them in table 1. It is clear from the table that the sensing response reported in our work is much better than the previously published results on H2 sensing.

Figures 8(a) and (b) shows the H2 response and recovery time curve (color strip in both curves indicates the time of the rGO-SnO2 NFs hybrid sensor. The response time is defined as the time required for the response to increase from its base value to 90% of its highest value. And the recovery time is defined as the time required for the response to decrease from 90% of its highest value to its initial value [19]. It was found that when the operating temperature was increased by 10 °C from RT the response time has decreased and the same trend was observed up to 60 °C. The rGO-SnO2 NFs showed a response time of 119.61 s at 60 °C for the concentration of 1000 ppm as compared to the pure rGO sample which showed the response time of 145 s. The recovery time of the hybrid sensor decreased monotonously as the operating temperature was increased from RT to 60 °C and it showed a recovery time of 265 s for 1000 ppm at 60 °C. The as-prepared pure rGO sample showed a recovery time of 275 s at the same operating parameters. A comparative study for the response
and recovery time of our sample with the already published literature shows that the sensing characteristics of our sample was much better than the previously published values (table 2).

For practical sensor applications, a sensor should be highly selective to various gases. We therefore verified the selectivity of RGO-SnO$_2$ NFs sensors upon exposing them to NH$_3$ for 200 ppm at operating temperatures RT, 40 °C and 60 °C respectively. For example, at 60 °C, the sensing response of our sample to H$_2$ is 19.6% whereas for NH$_3$ it is 15.96% (supplementary figure S3). The selectivity coefficient ($K = \frac{\text{Response}_{H_2}}{\text{Response}_{NH_3}}$) for H$_2$ to NH$_3$ at this operating condition was found to be 1.22 confirming the elective detection of H$_2$.

The higher sensing performance of the RGO-SnO$_2$ NFs hybrid composite can be attributed to three factors.

(i) The first and foremost factor is the way by which SnO$_2$ NFs gets structurally integrated with rGO to improve the available active sites for H$_2$ interaction. As seen in the FE-SEM images, the structural integration occurs in two ways, namely type 1 and type 2. In the type 1 hybrid structure, SnO$_2$ NFs protrude out of the rGO sheets and directly comes into contact with the H$_2$ molecules. The protruding nanorods create more open ends resulting in more active sites, such as vacancies, defects and unsaturated bonds which greatly facilitate the adsorption and diffusion of H$_2$. In the type 2 hybrid structure, SnO$_2$ NFs are covered by the rGO sheets which plays a significant role in preventing the aggregation of rGO sheets, which in turn increases the active surface area (figures 9(a) and (b)).

(ii) Secondly, there is a change in resistance due to the interaction between the oxygen molecules absorbed on SnO$_2$ and H$_2$ gas. When an O$_2$ molecule gets absorbed on the surface, it gets converted into a negative ion by the following reaction [21].

$$O_2(\text{air}) \rightarrow O_2(\text{ads}) \quad (4)$$
$$O_2(\text{ads}) + e^- \rightarrow O_2^-(\text{ads}) \quad (5)$$

When SnO$_2$ is exposed to a reducing gas such as H$_2$, the gas molecules react with the oxygen ions on the surfaces of SnO$_2$ NFs, as shown in the equation below. Such reactions result in the retrieval of the trapped electrons back to the conduction band of the sensing film and lead to a decrease in resistance of SnO$_2$ NFs (figure 9(a)).

$$2H_2 + O_2^-(\text{ads}) \rightarrow 2H_2O + e^- \quad (6)$$

### Table 1. Comparison of sensing performance of the H$_2$ sensor prepared in this work with those reported in the literature.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Reduced graphene oxide/SnO$_2$ nanoparticles</td>
<td>50°C</td>
<td>1000</td>
<td>3.2</td>
<td>2012 [31]</td>
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<tr>
<td>Graphene/ZnO nanocomposite</td>
<td>150°C</td>
<td>200</td>
<td>3.5</td>
<td>2014 [32]</td>
</tr>
<tr>
<td>Palladium loaded tungsten oxide nanoparticles</td>
<td>200°C</td>
<td>200</td>
<td>20</td>
<td>2013 [33]</td>
</tr>
<tr>
<td>Ni-doped TiO$_2$ nanotubes</td>
<td>200°C</td>
<td>1000</td>
<td>13.8</td>
<td>2013 [34]</td>
</tr>
<tr>
<td>Reduced graphene oxide</td>
<td>300°C</td>
<td>200</td>
<td>17</td>
<td>2013 [35]</td>
</tr>
<tr>
<td>Pd-loaded SnO$_2$ nanofibres</td>
<td>320°C</td>
<td>1000</td>
<td>12</td>
<td>2013 [36]</td>
</tr>
<tr>
<td>Pt-SnO$_2$ nanostructured composite thin film</td>
<td>85°C</td>
<td>150</td>
<td>7</td>
<td>2015 [37]</td>
</tr>
<tr>
<td>Pt/Pd bimetallic ultra-thin films</td>
<td>150°C</td>
<td>10 000</td>
<td>13.5</td>
<td>2016 [38]</td>
</tr>
<tr>
<td>ZnO:Cd nanorods</td>
<td>220°C</td>
<td>1000</td>
<td>6.13</td>
<td>2015 [39]</td>
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<tr>
<td>CVD grown graphene</td>
<td>130°C</td>
<td>10 000</td>
<td>7.6</td>
<td>2015 [40]</td>
</tr>
<tr>
<td>RGO-SnO$_2$ NFs</td>
<td>60°C</td>
<td>200</td>
<td>19.6</td>
<td>This work</td>
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Table 2. Comparison of response and recovery time of H₂ sensor prepared in this work with those reported in the literature.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Operating temperature (°C)</th>
<th>Concentration (ppm)</th>
<th>Response time (sec)</th>
<th>Recovery time (s)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Nanostructured molybdenum oxide</td>
<td>200°C</td>
<td>1000</td>
<td>270</td>
<td>—</td>
<td>[41]</td>
</tr>
<tr>
<td>CuO-Cu₃Feₓ₋ₓO₄ nanostructured thin films</td>
<td>295°C</td>
<td>1250</td>
<td>190</td>
<td>400</td>
<td>[42]</td>
</tr>
<tr>
<td>Pt/MoO₃ with La₂O₃ layer</td>
<td>180°C</td>
<td>1250</td>
<td>135</td>
<td>507</td>
<td>[43]</td>
</tr>
<tr>
<td>SnO₂ functionalized AlGaN/GaN</td>
<td>50°C</td>
<td>10000</td>
<td>240</td>
<td>570</td>
<td>[44]</td>
</tr>
<tr>
<td>Pd-WO₃ thick film</td>
<td>200°C</td>
<td>200</td>
<td>270</td>
<td>—</td>
<td>[45]</td>
</tr>
</tbody>
</table>
Figure 9. Schematic representation of the incorporation of SnO2 NFs into a rGO layer. (a) type 1 hybrid structure and (b) type 2 hybrid structure.

(ii) Thirdly, there is a formation of a heterojunction at the interface between the rGO and SnO2 NFs. Since the work function of rGO (4.75 eV) is higher than that of SnO2 (4.3 eV), as soon as a physical contact is formed between SnO2 NFs and rGO, electron flows from SnO2 NFs to rGO in order to align the Fermi level to reach an equilibrium state [5, 46, 47]. It results in the formation of a depletion layer or potential barrier at the RGO-SnO2 NFs interface. The width of the depletion layer changes due to interaction with H2 producing a noticeable change in resistance.

By considering all of these factors, the improved sensing characteristics of the rGO-SnO2 NFs can be explained as follows. On injecting the H2 gas, all these three types of interactions occur simultaneously on the surface of rGO-SnO2 NFs. The H2 molecules directly interact with (i) rGO layer ($R_{rGO}$) (ii) and SnO2 NFs ($R_{SnO2}$ NFs) and the (iii) rGO-SnO2 NFs interface ($R_{interface}$) which results in a modulation of their individual resistance contributing to the total change in resistance of the sensing layer resulting in improved sensing characteristics.

4. Conclusions

In summary, we have demonstrated a low temperature rGO-SnO2 NFs composite based H2 sensor fabricated by a simple drop-casting process. The surface morphology of the hybrid structure was characterized by a field emission scanning electron microscope (FE-SEM), demonstrating that incorporation of SnO2 NFs prevents the irreversible restacking of rGO. The sensing property of the rGO-SnO2 NFs hybrid structure was studied at different operating temperatures (RT, 40 °C, 50 °C and 60 °C) by exposing it to various concentrations of H2 ranging from 200 ppm to 1000 ppm. The as-fabricated rGO-SnO2 NFs hybrid structure exhibited an excellent response of 19.6% to 200 ppm of H2 at 60 °C which is 126% improvement compared to the pure rGO. The improved response was attributed to the enhanced active surface area provided by SnO2 NFs and the formation of a heterojunction at the rGO and SnO2 NFs interface. Our work suggests that the RGO-SnO2 NFs based hybrid composite can be a potential pathway to achieve a low temperature H2 gas sensor with better sensing performance than their constituents alone. This work demonstrates that the as-prepared rGO-SnO2 hybrid composite can be used for practical applications for monitoring H2 at temperatures as low as 60 °C. Currently, a systematic study on the effect of various concentrations of SnO2 NFs on further improving the sensing properties of rGO thin film is being carried out.

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