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Graphene oxide/SnO_2 nanocomposite as sensing material for breathalyzers: Selective detection of ethanol in the presence of automotive CO and hydrocarbons emissions

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Abstract. SnO_2 was ultrasonically deposited (precipitated) in the presence of different amounts of graphene oxide (GO) prepared by the modified Hummers' method. The resulting nanocomposites were used as sensing material for the detection of 1000 ppm CO and VOCs including ethanol, acetone and toluene, and CH_4 in a temperature range of 150-300°C. The nanocomposites were characterized by Raman spectroscopy, XRD, BET surface area measurement, FT-IR, and SEM methods. It seems that SnO_2 layers were deposited on the GO surface and incorporated into the matrix. This resulted in 47% increase in the nanocomposite BET surface area. The addition of 0.1 wt% GO to SnO_2 increased the response to CO by about 6 times at 300°C. 0.05 wt% GO as an optimum amount was included in SnO_2 up to 2-fold enhancement in response to ethanol, and toluene was observed. At 250°C, the highest response to ethanol was obtained, which is 120, 114, 1400, and 15 times larger than the responses to CO, toluene, methane and acetone, respectively, making the sensors quite selective to ethanol. Furthermore, this sensor exhibited good response in the low concentration of ethanol.

1. Introduction

Graphene was discovered in 2004, and K. Novoselov and A. Geim received the Nobel Prize in physics for their fundamental experiments on graphene in 2010 [1]. Graphene has a two-dimensional structure of carbon with a carbon–carbon bond length of 0.142 nm. The combination of large thermal conductivity, unique electrical properties, and large surface area [2] makes graphene and its derivatives a promising material for many applications, including lithium-ion batteries [3], transistors [4], fuel cells [5], and sensors [6].

Volatile Organic Compounds (VOCs) are the most important indoor pollutants emitted from various sources such as cleaning supplies, cosmetics, pesticides, and office equipment. VOCs present in an indoor environment are considered as the main cause of the Sick Building Syndrome (SBS) [7].

Chemical gas sensors utilizing semiconductor metal oxides, such as SnO_2, ZnO, and Fe_2O_3, are the most promising devices due to the low fabrication cost, simplicity in practical application, low weight and fast response to a wide variety of VOCs, and pollutant and

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toxic gases. Among metal oxides, SnO_2 is well known for the detection of different pollutants. The band gap of SnO_2 is 3.6 eV. SnO_2 has excellent electrical properties and high chemical stability. Although the exact mechanism of gas sensor behavior is not well known, it is basically the resistance change upon adsorption of oxygen [8]. SnO_2-based gas sensors typically operate by monitoring changes in surface conductivity. Oxygen species, mainly in the form of O^-, are generated by dissociative chemisorption of oxygen molecules on SnO_2 surface followed by electron depletion from the surface, resulting in a decrease in conductivity [9].

Recently, graphene or graphene quantum dots have been utilized for fabrication of chemical gas sensors [10,11]. This is because graphene has special features such as large specific surface area, high carrier mobility at room temperature, and low electrical noise [11]. Furthermore, graphene decreases the sensing temperature and, therefore, lowers the energy consumption.

On the other hand, in recent years, researchers have focused on improving the stability and selectivity of the sensing materials for detecting VOCs by the addition of other semiconductors and insulators to the base semiconductor. While there are several reports on the use of semiconductor oxides for detection of VOCs [12-14], there is no significant amount of the related literature review on SnO_2/GO nanocomposites for this purpose. Zhang et al. used SnO_2/reduced graphene oxide nanocomposites for detecting NO_2 [15]. Song et al. examined this nanocomposite for H_2S sensing at room temperature [16]. Also, Xiao et al. reported the use of hydrothermal method for SnO_2 modified by reduced graphene oxide (rGO) for detection NO_2 in trace concentrations [17]. Detection of acetone and hydrogen sulfide in exhaled human breath by SnO_2 nanofiber decorated on rGO nanosheets was done by Choi et al. [18].

In this work, GO/SnO_2 nanocomposites are synthesized by an ultrasonic deposition-precipitation method, and their gas sensing properties for the detection of toxic/combustible gases and VOCs are investigated.

2. Experimental

2.1. Synthesis of sensing materials

Graphene Oxide nanosheets were prepared by the improved Hummers' method [19]. Graphite flakes were added to a mixture of 9:1 H_2SO_4/H_3PO_4. $KMnO_4$ was added slowly while stirring. The mixture was then heated at 50°C and stirred for 48 h. H_2O_2 was added to the brown mixture, then washed with deionized water (HCl) and ethanol several times, and dried at room temperature.

SnO_2 was prepared via an ultrasonic deposition-precipitation method. Details of this method have been described elsewhere [10]. Briefly, for 0.05 and 0.1 wt% GO/SnO_2 nanocomposites, GO was dispersed in 0.15 M $SnCl_4$ aqueous solution and ammonia as the precipitating agent was added while sonicating. The precipitate was collected, washed with deionized water several times, and dried and heated at 400°C for 1.5 h. For the sake of brevity, hereafter, pure SnO_2, 0.05 and 0.1 wt% GO/SnO_2 nanocomposites are denoted as S, SG5, and SG10, respectively.

2.2. Characterization of the sensing materials

The morphology of GO and GO/SnO_2 nanocomposites was characterized using a field emission scanning electron microscope (FE-SEM) operating at 20.0 kV by JSM 6700F-JEOL. Crystal structure of the powders was recorded with X-Ray Diffraction (XRD) using a Philips PW1800 apparatus. Specific surface areas of the samples were determined by the Brunauer-Emmet-Teller (BET) method with a Quantachrome CHEMBET 3000. The Fourier-Transform Infrared (FT-IR) spectra of the samples were measured using a Bruker VECTOR 22. Raman spectra of the powders were obtained by Bruker SENTERRA equipment. Morphology of the synthesized GO was investigated using transmission electron microscopy (TEM; Philips, CM120).

2.3. Fabrication of the sensors

Sensing materials were mixed with deionized water to form a thick paste. This paste was then screen printed on alumina substrates previously coated with Au electrodes. The fabricated sensor was dried and annealed at 400°C for 1.5 h.

The performance of the sensors for the detection of target gases was measured by a test setup composed of Mass Flow Controllers (MFCs) to adjust concentration of the target gas in air, furnace equipped with PID temperature controller, sensor holder and electronic board for measuring resistance/conductance of the sensor. The target gas with proper concentrations was introduced into a glass reactor, whose temperature was adjusted by the temperature controller. The sensors were exposed to 1000 ppm ethanol, CO, toluene and acetone; 5000 ppm CH_4 and instantaneous resistance changes were monitored. Finally, the sensors' responses, defined as (Ra/Rg-1), versus the temperature in the range of 150-300°C were studied. Ra is the sensor resistance in air and Rg is its resistance in the presence of the target gas.

3. Results and discussion

3.1. Characterization

BET surfaces areas of S, SG5, and SG10 are 64, 93, and 94 m^2/g, respectively. About 47% increase in the BET surface area is observed upon the addition of GO to

SnO_2. GO surface may comprise numerous nucleation centers [20] for the formation of SnO_2 nanoparticles when a ultra-sonicated deposition-precipitation procedure is applied to the preparation of the samples. In this way, SnO_2 nanoparticles' sizes decrease and lead to an enhancement in the BET surface area.

The TEM and SEM micrographs of GO and SG5 are shown in Figure 1. As is evident from Figure 1(a) and (b), the transparency, as compared to the background, indicates that the synthesized GO comprises 1-5 layers of graphene in good agreement with other reports [21]. Figure 1(c) shows the SEM micrograph of the SnO_2/GO nanocomposite. It seems that SnO_2 nuclei are formed on the GO nanosheets in the sonication process and cover the GO sheets, in addition to the formation of SnO_2 nanoparticles in bulk solution making SnO_2 matrix.

Figure 2 shows XRD patterns of SnO_2, SG5, and SG10. The diffraction peaks corresponding to (110) at 26.56°, (101) at 32.28°, and (211) at 51.49° belong to the tetragonal rutile structure of SnO_2 (JCPDS File No. 41-1445) [22]. The specific diffraction peaks of GO 20° [23] are not observed. This can be related to too low concentrations of GO to be detected by XRD.

Figure 2 also demonstrates that by increasing the amount of GO in the nanocomposite samples, the XRD patterns exhibit weaker peaks of (110) and (211) planes, while the peak intensity of (101) plane is enhanced. Moreover, by increasing GO content, the full widths at half-maximum (FWHM) increase, suggesting that GO nanosheets act as crystallite growth inhibitors for SnO_2 crystals.

Figure 3 shows the Raman spectra of GO and SG5 in 400-3500 cm^{-1} range. The appearance of a 2D peak at 2740 cm^{-1} and the overtone of D band imply that the GO contains a few layers [24]. D-band peak at 1360 cm^{-1} is indicative of defects in the crystalline structure of the graphite. The peak that corresponds to E_{2g} phonon at the central zone of the Brillouin zone is at 1600 cm^{-1}. The peak at about 670 cm^{-1} corresponds to O-Sn-O vibrations. The FTIR spectrum of GO, presented in Figure 4, confirms the C-O, C=O and O-H (C-OH, COOH, H_2O) bonds in GO sample. The carboxylic groups are almost at the edge of planes and epoxy groups are usually formed on the surface [25]. C-O bonds may be attributed to the epoxy functional groups present on the basal plane of GO. O-Sn-O vibration is observed at about 700 cm^{-1} in the spectra which is also attributed to SnO_2 [26].

3.2. The sensing properties

The responses of SnO_2, SG5, and SG10 toward 1000 ppm ethanol, CO and toluene in the air as a function of temperature are presented in Figure 5. The insets of diagrams show the response toward GO content at various temperatures.

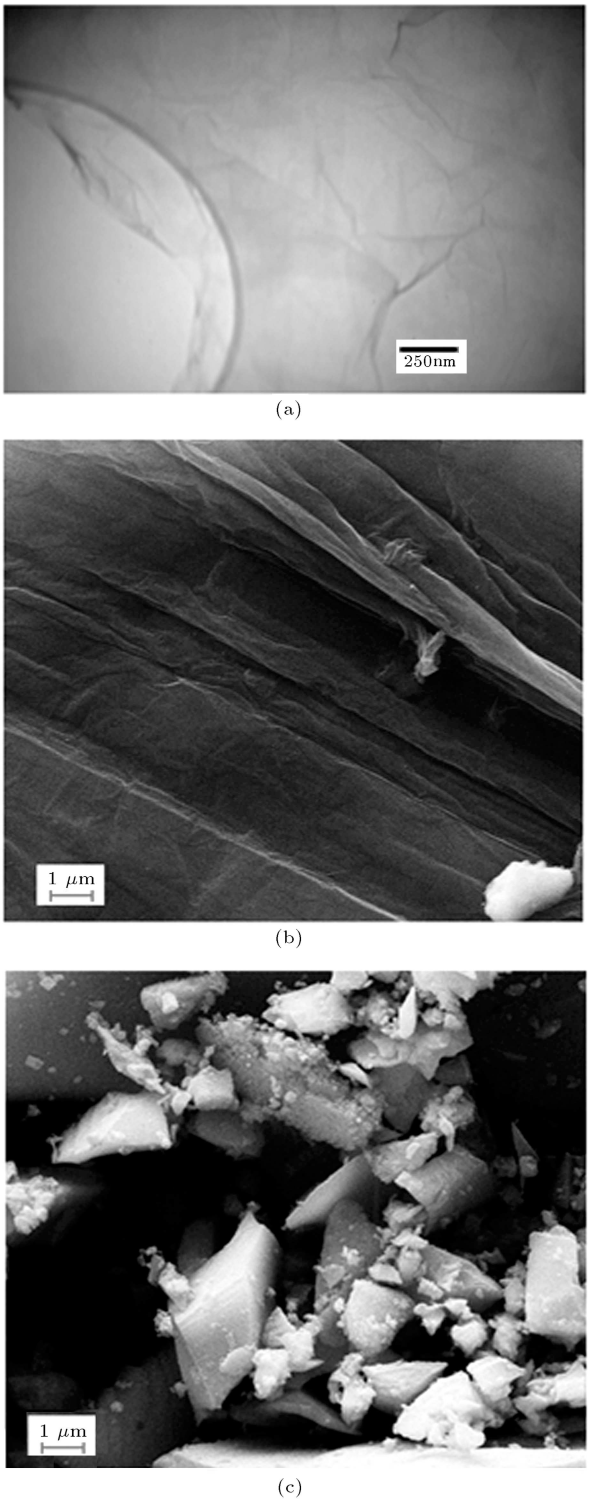


Figure 1. The TEM (a) and SEM (b) micrographs of GO, and SEM of SG5 (c) containing 0.05 wt% GO in SnO_2.

For most gases, the response versus temperature has a somehow volcano-type behavior. This behavior seems to be the result of the competition between surface reaction and adsorption and diffusion on the surface and into the sublayers of the surface, respectively [27]. By the addition of 0.05% GO to SnO_2, the

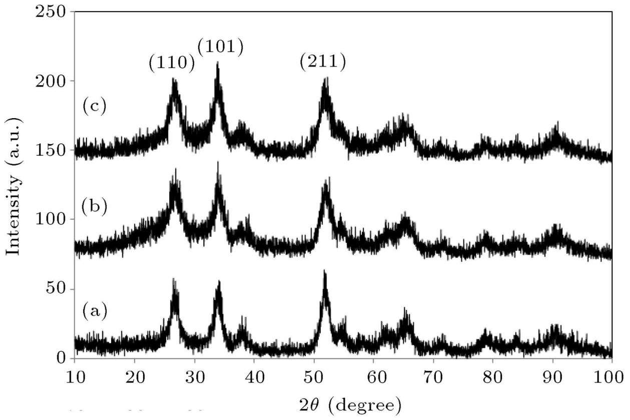


Figure 2. The XRD patterns of (a) blank SnO_2, (b) SG5, and (c) SG10.

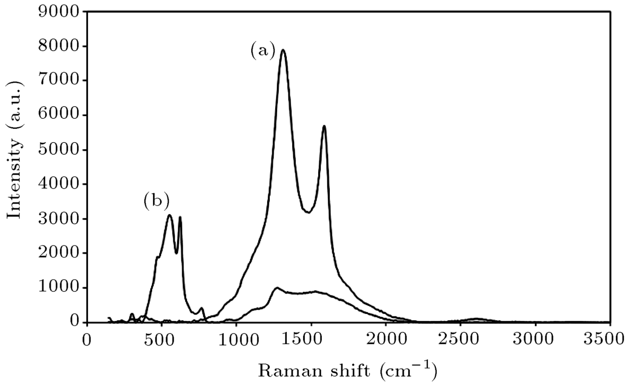


Figure 3. The Raman spectra of (a) GO and (b) SG5.

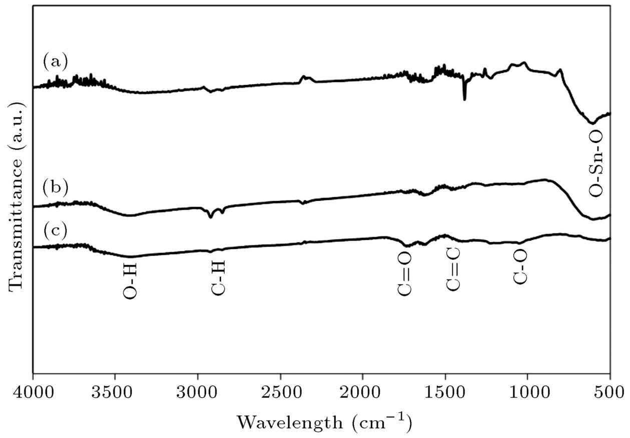


Figure 4. FTIR spectra of (a) blank SnO_2 (b) SG5 and (c) GO.

response to ethanol and toluene increases compared to pure SnO_2 (Figure 5(a)-(c)). The maximum responses of SG5 to both ethanol and toluene are obtained at 250°C, which are about 1.3 and 1.2 times larger than those of the pure SnO_2, respectively. At 300°, the responses increase by a factor of 2 for ethanol and about 5 for toluene. The responses of SG10 to toluene at 150 and 300° are 1.4 and 6.5 times larger than

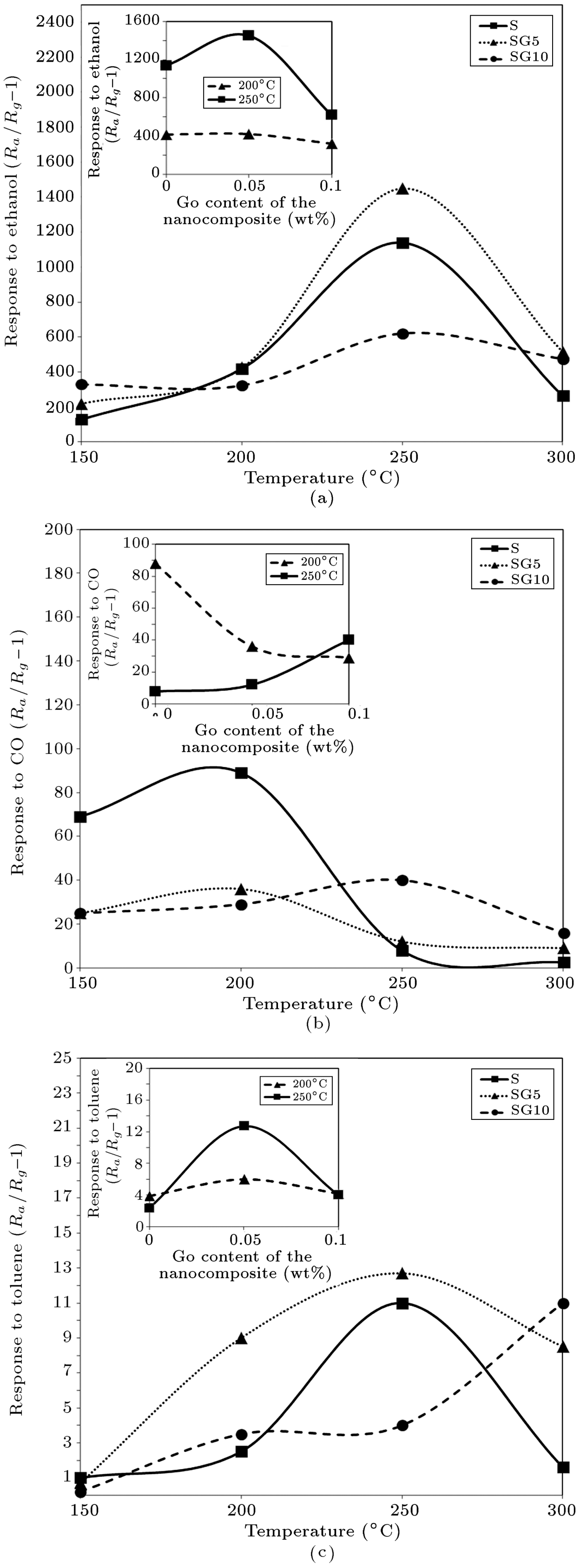


Figure 5. The sensors' responses to 1000 ppm: (a) Ethanol, (b) CO, and (c) toluene in the air as a function of temperature.

those of blank SnO_2, respectively. As GO is added to SnO_2, the sensor's response to CO decreases at low temperatures, while the response significantly increases at higher temperatures. For instance, the addition of 0.05 and 0.1 wt% GO to SnO_2 at 250° increases the response by factors of 1.5 and 5.1, respectively.

The response of the sensor to ethanol is much higher than those to toluene and CO. This is most likely due to the mechanism of reactions taking place on the surface of the sensor. When a target gas is exposed to the sensor, it reacts with the oxygen species on the surface, mainly in the form of O^-. This interaction results in the electron being transferred into the conduction band of the semiconductor, and thus, the resistance of the sensor decreases. However, the number of electron transfer and the time constant of this interaction are considered to be among the parameters affecting the performance of the sensor including sensitivity and response time.

As compared to toluene, ethanol and CO are small molecules; thus, their diffusion and adsorption on the surface are easier (Molecular weight of toluene, ethanol, and CO are 92.14, 46, and 28, respectively.) On the other hand, the lower amount of toluene is weakly adsorbed on the sensor's surface because of steric hindrance of its aromatic ring [9]. Possible chemical reactions for the target gases at the surface can be described as follows [28]:

$$CO + O^- \rightarrow CO_2 + e^- \qquad (1)$$

$$C_2H_5OH + 6O^- \rightarrow 2CO_2 + 2H_2O + 6e^- \qquad (2)$$

$$C_6H_6CH_3 + 18O^- \rightarrow 7CO_2 + 4H_2O + 18e^- \qquad (3)$$

Based on these equations, the reaction of one ethanol molecule with surface oxygen would release 6 electrons into the semiconductor conduction band compared to one electron per carbon monoxide molecule. This may explain the dramatically larger responses to ethanol [28]. On the other hand, although the toluene would release even more electrons, the diffusion onto the surface and the oxidation reaction may be more difficult due to its aromatic ring [29].

GO in its nanocomposite with SnO_2 enhances the responses to different gases through increasing the rates of diffusion and adsorption on sensing layer and forming a heterostructure of p-n junctions between GO and SnO_2. There are at least 3 kinds of interfaces in the sensing material: interface between the SnO_2 grains, between the GO sheets, and between the SnO_2 grains and GO sheets. GO acts as a p-type, while SnO_2 is an n-type semiconductor; therefore, depletion regions at the interface between SnO_2 and GO and on the surface of SnO_2 grains are formed. Eventually, the response is enhanced due to the amplification effects of junction structure combined with the surface reactions of the target gas. This phenomenon has been observed and reported by other groups [30,31]. However, the exact mechanism of sensing has not been fully understood yet and needs further investigations.

Figure 6 shows the responses of SG5 towards 5000 ppm methane and 1000 ppm acetone. The response of the sensor to acetone is up to more than two orders of magnitude higher than its response to methane. Figure 7 shows the selectivity, at 250°, of the sensor to ethanol defined as its response to ethanol divided into its response to another gas. The selectivities of SG5 to ethanol with respect to methane, CO, and toluene are about 1800, 120 and 114, respectively. This indicates that SG5 is a selective sensor to ethanol in the presence of the other gases. Therefore, the sensor may be used as a breathalyzer to selectively detect ethanol in the presence of automotive emissions including CO and hydrocarbons.

The variation of the response of SG5 sensor to various concentrations of ethanol at 250°C is shown in Figure 8. It is interesting to note that the response of SG5 to ethanol concentration as low as 50 ppm is 22.5.

The normalized transient responses of the SG5

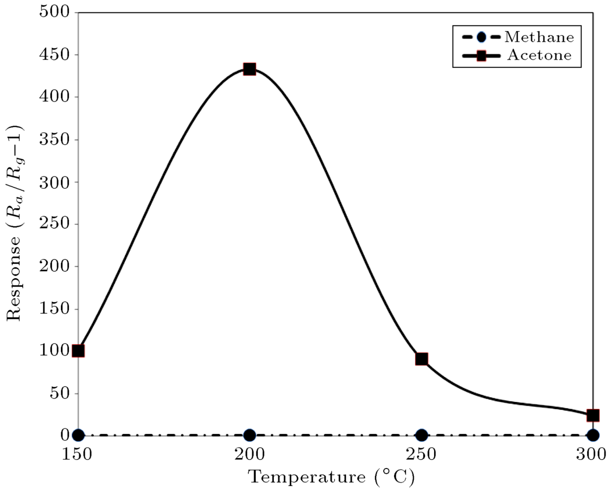


Figure 6. The response of SG5 towards 5000 ppm methane and 1000 ppm acetone.

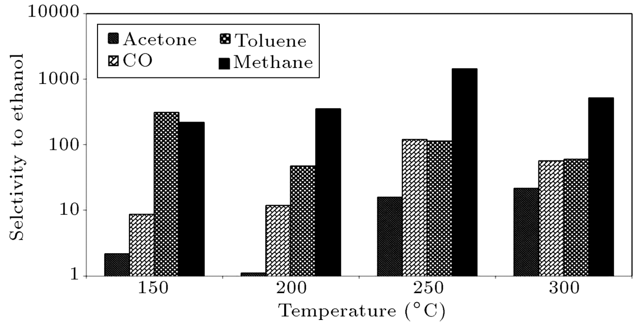


Figure 7. Selectivity of SG5 sensor to ethanol with respect to methane, CO, and toluene.

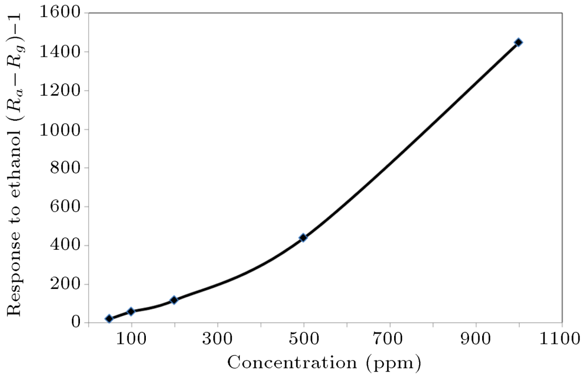
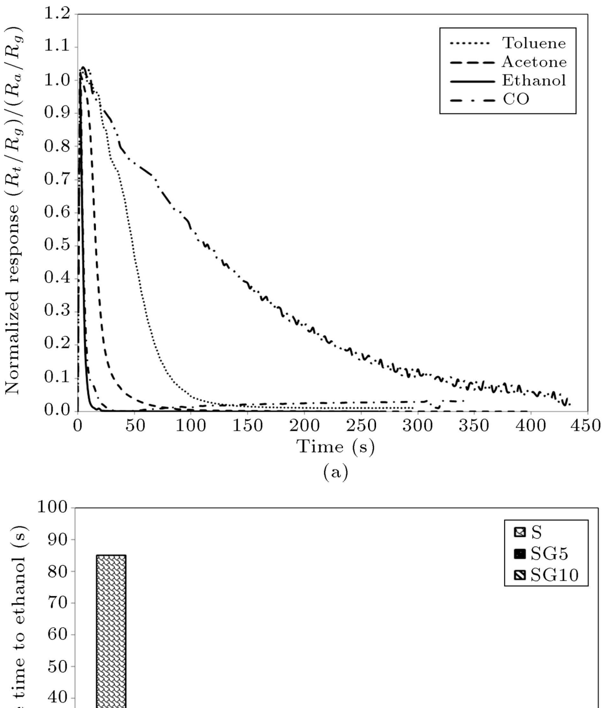


Figure 8. Responses of SG5 sensor to various concentrations of ethanol at 250°C.



(a)

(b)

Figure 9. (a) Normalized transient responses of SG5 to various gases at 250°C. (b) Response times of the sensors containing various amounts of GO to 1000 ppm ethanol at different temperatures.

sensor to various gases at 250°C are shown in Figure 9(a). The normalized transient response is defined as $(R_t - R_g)/(R_a - R_g)$, where R_t is the sensor's instantaneous resistance, and R_a and R_g are the stable resistances in the air and the target gass, respectively. Figure 9(b) shows various sensors' response times to ethanol at different temperatures. The response time is defined as the time required for the sensor to reach 90% of its final response. According to Figure 9(a), relatively fast and similar responses to CO and ethanol are observed. These compounds have one oxygen atom in their structure that can facilitate the reaction of their adsorbed species with the surface oxygen species [9]. SG5 sensor's response to acetone and toluene lags behind that of ethanol, and the most sluggish response is observed for methane. The response times of SG5 at 250°C for CO, ethanol, acetone, and toluene are 8, 8, 31, and 83 s, respectively. This may show the relative rates of diffusion through the sensing layer and adsorption and reactions on the sensor surface of the gases. The differences in response times are believed to be following the two-film theory [32]. Based on this theory, when a sensing layer is in contact with air, the gas film is formed between the gas phase and the solid. The driving force for the gas diffusion through the film is managed by the difference of gas concentration at the solid surface and concentration in the gas phase-gas film interface. Some reactive gases, e.g., CO, diffuse across gas film and are oxidized immediately, while some other gases do not have this ability and have to be dissociated from atoms prior to being reacted on the surface [32].

Figure 9(b) indicates that as 0.05 wt% GO is added to its nanocomposite with SnO_2, the response time significantly decreases due possibly to an enhancement of the surface area and the larger concentration of adsorbed oxygen species on the surface. Further addition of GO has minor effects on lowering the response times. However, the response times for all the sensors pass a minimum at 250°C.

4. Conclusion

In this study, graphene oxide was prepared by improving Hummers, method, and SnO_2 particles were deposited on the graphene oxide sheets. Moreover, effects of the addition of low amounts of graphene oxide (GO) to SnO_2 on different characteristics of the resulting nanocomposite and detection of various volatile organic compounds (VOCs), CO, and CH_4 were investigated.

The Raman spectrum and TEM micrograph of the GO show the formation of 1-5 layers of graphene nanosheets. The carboxylic groups on GO nanosheets may act as nucleation centers for ultrasonic deposition-precipitation of SnO_2 and significantly enhance the BET surface area. P-n junction may also be formed at SnO_2-GO interface which in turn creates two depletion layers. As compared to SnO_2, 0.05 wt% GO-SnO_2 sensor (SG5) shows about 2 times larger response than those of both ethanol and CO, while the response to toluene is enhanced by 3.6 times on the 0.1% GO-SnO_2 sensor. The ratios of SG5 sensor's response to ethanol to responses to methane, CO, and toluene at 250° are about 1400, 120 and 115, respectively. This indicates that SG5 is a selective sensing material for ethanol in the presence of the other gases. SG5 also shows significantly lower response times to ethanol than SnO_2 due possibly to an enhancement in the surface area, gas diffusivity, and adsorbed oxygen concentration. GO-SnO_2 nanocomposite is suggested to be utilized in the fabrication of breathalyzers to selectively detect ethanol in the presence of automotive emissions including CO and hydrocarbons.

Acknowledgment

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