

Room-Temperature SO₂ Gas Sensing Properties of the Ag@GO Heterogeneous Nanomaterial

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Abstract

The study proposes SO₂ gas sensor based on a quartz crystal microbalance (QCM) coated with Ag@GO heterogeneous nanomaterial at room temperature. The heterogeneous nanomaterial was synthesized by hydrothermal method at 160 °C for 90 min. The structure and morphological characteristics were analyzed by using field-emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy. The Ag@GO heterogeneous nanomaterial was dispersed in water and coated on an Au electrode of QCM via spray coating method. The fabricated sensor exhibits a good response to SO₂ in the concentration range of 2.5-15 ppm. The highest gas sensitivity of the sensor is 8.98 Hz/ppm corresponding to the adsorbed SO₂ mass density of 2.38 μg.cm⁻². The gas sensing results indicated that the developed sensor can be applied for monitoring, warning, and controlling SO₂ in the environment. Moreover, the gas adsorption properties of Ag@GO nanomaterial can also be considered for a filter to remove toxic gases in respirators and environmental treatment.

Keywords: Ag@GO, GO, gas sensor, QCM, SO₂.

1. Introduction

Sulfur dioxide (SO₂) is one of seven toxic inorganic gases, which are formed during the combustion of finished products derived from fossil fuels. SO₂ is known as a colorless gas and the main cause of acid rain and affects human health seriously even at low concentrations. For example, as stated in Air Quality Guidelines (AQG) by World Health Organization (WHO) in 2006, the exposure short-term (24 hours) of AQG level is 40 μg/m³ [1]. In addition, American Conference of Governmental Industrial Hygienists (ACGIH) in 2005 Threshold Limit Values and Biological Exposure suggested the Threshold Limit Value - Time-Weighted Average (TLV-TWA) and Threshold Limit Value - Short-Term Exposure Limit (TLV-STEL), these values are 2 ppm and 5 ppm, respectively [2]. Namely, a concentration of 2 ppm is not expected to cause side effects for most workers when they are repeatedly exposed to it for 8 hours a day or 40 hours a week. Workers will also not experience irritation, chronic or irreversible tissue damage, when they are exposed to 5 ppm of SO₂ concentration for a short period of time. However, a concentration of more than 5 ppm can result in airway resistance or even death for most people [3]. Therefore, the development of materials with good SO₂ adsorption properties and pollution monitoring sensors is an important task to scientists in the world. Hence, in-depth studies on the fast adsorption rate and high selectivity of SO₂ are

suitable and necessary, such as the mass-type gas sensor [4], the flue gas desulfurization or capture [5], and the SO₂ resistance of catalyst/sorbent for mercury removal [6]. Moreover, there are many studies on the various SO₂ gas sensors, including Micro-Electro-Mechanical Systems sensors, conductivity sensors, and mass change sensors. Among them, a mass-type sensor exposes a good sensing property as highly sensitive and room temperature operation. The mechanisms of the mass-type sensor are typically based on the change in resonant frequency of a quartz crystal microbalance (QCM) with the change in the mass of the target gas molecules that absorb on the sensing material layer. Thus, to investigate the SO₂ adsorption properties of materials efficiently, the QCM is considered a reliable method thanks to its high resolution, stability as well as low energy consumption. The QCM resolution is less than 1 nanogram/cm². The dependence on temperature of QCM sensor is negligible (≈ 1-3 Hz/°C), and this effect was generally ignored by the adsorption/desorption processes for gas phase of monolayer [7].

The QCM's electrodes are typically made of precious metals such as Au or Ag which are not highly appreciated for adsorption capacity. Hence, the active electrode of the QCM is often improved by coating a sensing material layer with high adsorption capacity of the target gases. Typical materials can be mentioned as

Metal-Organic Frameworks (MOF) KAUST 7&8. Both QCM sensor based on two MOFs show higher detection capacity than 25 ppm that can cause nose and eye irritation [8]; polyanilines have the unique gas sensing properties in the concentration range of 50 - 250 ppm and they are adsorbing materials at high concentration from 500 to 1250 ppm [9]; on the other hand, multi-walled carbon nanotubes and iron oxide expose a good sensing layer for SO₂ at low concentrations (lower than 20 ppm) and fast response/recovery times (about 100 s). However, the sensitivity of γ -Fe₂O₃ nanorods is not excellent with the maximum value of 2.15 Hz/ppm [10, 4]. In addition, carbon material groups such as CNT, graphene, graphene oxide (GO), reduced graphene oxide (rGO) or GO's derivatives are also widely used for the QCM sensors. In general, large surface area, defect richness, electron transfer efficiency and heterojunction have strongly contributed to their adsorption/desorption kinetics. Nevertheless, most of these studies focus on moisture (RH) and organic/inorganic gas detection sensors with short response/recovery time. A mini review of Fika Fauzi and colleagues on the QCM sensors based on monolayer graphene, rGO, rGO/SnO₂, rGO/SnO₂/Ag NPs show low limit of detection (LOD) and good sensitivity for Ethanol, Acetone, and NO₂. Furthermore, the GO composite coated sensor exhibits fast response, good repeatability, and excellent long-term stability in 30 days when it exposes to trimethylamine concentration from 10 to 75 ppm [11]. In particular, the potential of GO nanomaterial in gas sensing application is not only proven by experiment but also theory. The researches on density functional theory (DFT) and the first-principles calculations also demonstrate that GO nanomaterial combined with Au or Fe nano particles increases the adsorption potential of toxic gas molecules (NO, CO, HCN and SO₂) [12, 13].

Based on the above literature survey, in this report, we focus on the synthesis of Ag@GO heterogeneous nanomaterial by a hydrothermal method. Moreover, the gas sensing and SO₂ adsorption properties of the Ag@GO were also investigated at room temperature. The SO₂ adsorption characteristics will be analyzed through the QCM sensor coated with Ag@GO heterogeneous nanomaterial. The change in mass on the active electrode of the Ag@GO sensor is caused by the continuous adsorption and desorption of SO₂ during the aerodynamic measurement. Additionally, the high repeatability, low limit of detection and short response/recovery times will be discussed in this research.

2. Experiment

2.1. Starting Raw Materials

Graphene oxide (GO, 99%) was purchased from Sigma-Aldrich corporation in Vietnam. Analytical-grade silver nitrate (AgNO₃, 99.9%), ammonium hydroxide (NH₃, 25%) and polyvinylpyrrolidone (PVP

(C₆H₉NO)_n, 95%) were purchased from Shanghai Chemical Reagent Co.Ltd (China); Acetone (CH₃COCH₃, 99.5%) and Ethanol (C₂H₅OH, 99.7%) were provided by Xilong Scientific Co., Ltd and Guangdong Guanghua Sci-Tech Co., Ltd, respectively. Deionized water (DI) was used in all experiments.

2.2. Hydrothermal Synthesis of Ag@GO

A schematic illustration of the synthesis of Ag@GO heterogeneous nanomaterial synthesized by the hydrothermal method is presented in Fig. 1. The specific process was described as follows: 85 mg of silver nitrate AgNO₃ and 50 mg of PVP were dissolved in 47.5 ml of DI in the ultrasonic tank for 30 min. Then, 20 mg of GO was dispersed into the solution of AgNO₃ and PVP, magnetically stirred for 30 min, to obtain A solution. After that, 2.5 ml of 25% NH₄OH solution was added into solution A slowly for 10 min until the pH of the solution reached 9 and stirred well with the aid of a magnetic stirrer to obtain B solution. When the reaction was completed, 50 ml of the obtained B solution was then poured out a Teflon autoclave for hydrothermal process. The hydrothermal process was carried out for 90 min at 160 °C. After cooling down naturally, the solution was removed impurities by a centrifugation at 4000 rpm for 20 min. Finally, the solution contained Ag@GO heterogeneous material was obtained with yellow brown.

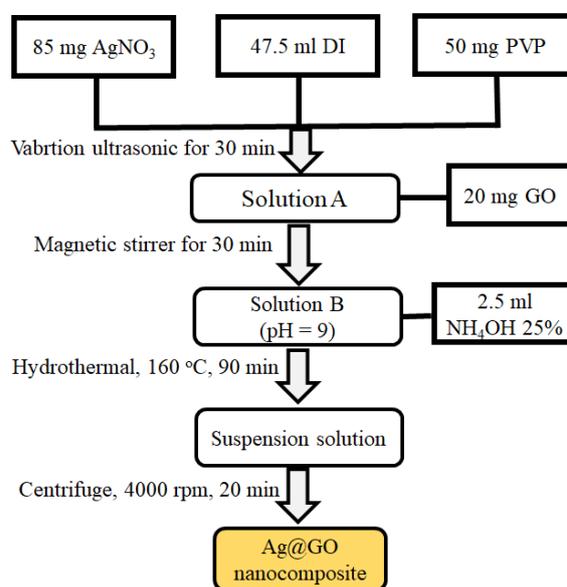


Fig. 1. Schematic illustration of the synthesis of Ag@GO heterogeneous nanomaterial

2.3. Preparation of QCM

The solution of Ag@GO heterogeneous nanomaterial was diluted in DI with the ratio of 1:4. The diluted solution was then sprayed on the active electrode of QCM to form a sensing layer. The spray coating process was described in detail as follows: first, the electrodes of QCM were cleaned with DI and

ethanol by using ultrasonic vibration for 5 min. Then, the QCM was dried by N₂ flow and stuck on a hot plate. The spray gun was placed about 20 cm away from the electrode surface. 5 ml of the prepared Ag@GO solution was sprayed on the active electrode of QCM at the rate of 0.2 ml/min. Finally, the Ag@GO coated QCM sensor was continued to be annealed at 175 °C for 60 min to evaporate solution and increase the adhesion of the material to the electrode.

2.4. Characteristics and Measurement

The crystallographic phases of the GO and Ag@GO were investigated by X-ray diffraction spectroscopy (XRD, Bruker D5005) using Cu K α radiation ($\lambda = 0.15406$ nm) and Raman spectroscopy (LabRAM HR 800, HORIBA JOBINYVON). The morphology and size distribution of the material were observed by transmission electron microscopy (TEM, JEOL-JEM 1010).

The gas sensitivity characteristics of the QCM sensor coated with Ag@GO were investigated by a self-made gas measuring system. The quartz crystal microbalance digital controller (QCM200) and 5 MHz Crystal Oscillator (QCM25) were connected to the computer through the SRSQCM200 software to measure the resonance frequency. The relationship between the resonant frequency shift of the sensor (Δf in Hz) and the mass change on the electrode (Δm in $\mu\text{g cm}^{-2}$) was studied and calculated by Sauerbrey equation [14] as shown in the following formula:

$$\Delta f = -C_f \Delta m \quad (1)$$

In this case, the 5-MHz-AT-cut QCM with $C_f = 56.6 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$ was used.

The experimental test of gas sensing properties is described in full cycle as follow: firstly, N₂ flow of 200 sccm rate was kept constant and blown into the testing chamber, 200 sccm rate is considered as a balance testing gas flow. The baseline of resonance frequency is obtained for 90 min. Secondly, N₂ flow was replaced by SO₂/N₂ flow with a ratio of $x/(200 - x)$. The SO₂ concentration (Con.) in ppm was determined as $x*100/200$, the specific values of test concentration are 2.5/5/7.5/10/12.5/15 ppm corresponding to 5/10/15/20/25/30 sccm of x , respectively. The duration of the SO₂ sensing examination of the QCM sensor based on Ag@GO heterogeneous nanomaterial was carried out for ~120 min. The instantaneous resonance frequency was recorded and used to calculate the frequency shift of sensor at the single concentration. Finally, 200 sccm rate of SO₂/N₂ flow was replaced by pure N₂ flow at the same rate until the resonance frequency of QCM sensor recovered to the baseline. The repeatability property was investigated for 3 - 5 fully cycles.

3. Results and Discussion

3.1. Morphology, Structure and Properties of Ag@GO Heterogeneous Nanomaterial System

The surface morphology and size distribution of the synthesized Ag@GO were analyzed using TEM as shown in Fig. 2. The TEM image confirms the presence of nanoparticles on the GO flakes in the Ag@GO heterogeneous nanomaterial system (Fig. 2a). The particle size estimated by TEM image was about 13 nm. The result indicates that the Ag@GO heterogeneous nanomaterial was formed by the hydrothermal process.

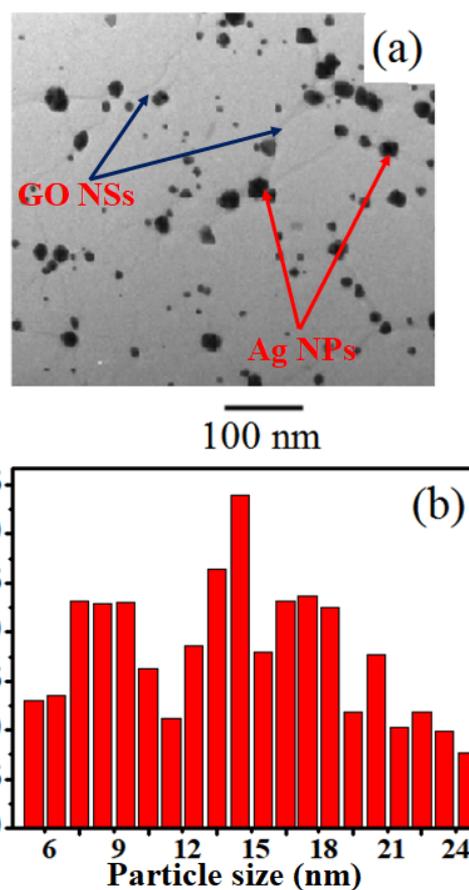


Fig. 2. (a) TEM image and (b) Size distribution of the Ag@GO synthesized by hydrothermal method.

The crystal structure of GO and Ag@GO materials is determined experimentally by XRD spectrum as shown in Fig. 3. It can be seen from the X-ray diffraction pattern in Fig. 3a that the GO sample exhibited a very high intensity peak at the position of 2θ equal to 10.9° corresponds to the lattice plane (001) [15]. As observed in Fig. 3b, the Ag@GO sample shows three strong diffraction peaks at 2θ of 38.2° , 44.4° , 64.5° , corresponding to crystal planes of (111), (200), and (220) (JCPDS No. 04-0783), which indicates the face-centered cubic structure, monophasic and polycrystalline Ag material. Moreover, the typical diffraction peaks of GO were not observed in the

Ag@GO sample, probably because the GO's diffraction peak is weaker, so it is covered by silver nanoparticles. Furthermore, the GO's main diffraction peaks can both decrease in intensity and shift towards a smaller 2θ angle which is probably because Ag nanoparticles are sandwiched among GO sheets or functional groups on GO sheet surface are removed during hydrothermal process to form reduced GO sheet (rGO) [16].

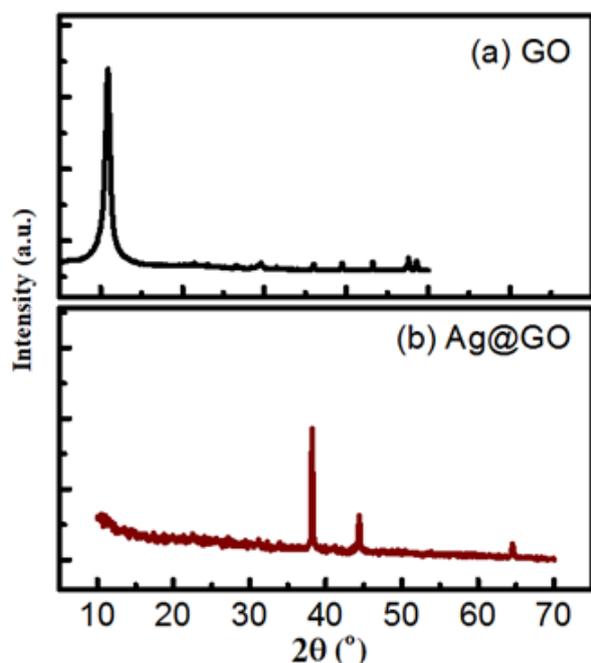


Fig. 3. XRD patterns of the pure GO (a) and synthesized (b) Ag@GO fabricated by hydrothermal method.

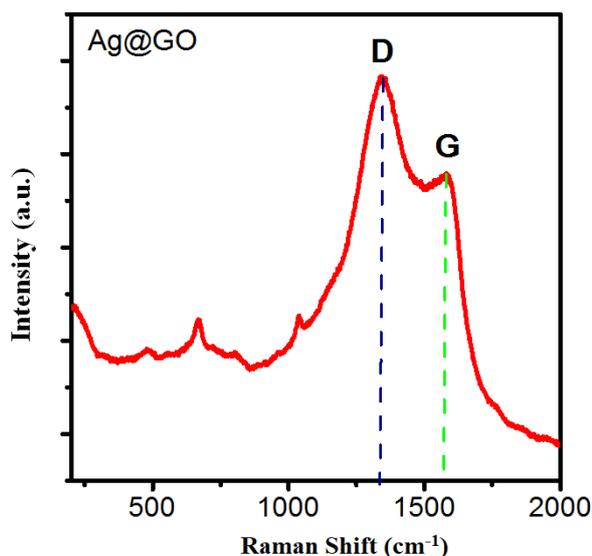


Fig. 4. Raman spectrum of the as-synthesized Ag@GO heterogeneous nanomaterial.

To confirm the presence of GO in the Ag@GO material, the Raman scattering was investigated. The

results of Raman spectroscopy of the Ag@GO nanomaterial are shown in Fig. 4. It is clearly observed that two active Raman modes around 1344 cm^{-1} and 1583 cm^{-1} are corresponded with D peak and G peak, respectively. The D and G peaks of GO are assigned to the A_{1g} and E_{2g} oscillation modes, respectively [17]. Thus, this result indicates the appearance of GO in the synthesized Ag@GO heterogeneous nanomaterial.

3.2. SO₂ Gas Adsorption Characteristics of Ag@GO Heterogeneous Nanomaterial Using QCM

To determine the SO₂ adsorption characteristics of Ag@GO heterogeneous nanomaterial, the resonant frequency shift of the QCM sensor was examined when the sensor was exposed to the target gas, similar to experimental method in our previous study [10], [18]. First, the response-recovery characteristics of the QCM sensor coated with Ag@GO material were investigated with SO₂ gas at various concentrations. Dynamic recovery-response curve of the Ag@GO-based QCM sensor with SO₂ in the concentration range from 2.5 to 15 ppm is described in Fig. 5a. The results reveal that the Ag@GO sensor responds well (shown by the sensor's resonant frequency shift) to SO₂ in the investigated concentration range. Specifically, at concentrations of 2.5, 5, 7.5, 10, 12.5, and 15 ppm, the sensor's frequency shift is -8.2, -33.8, -58.5, -82.7, -105.4, and -134.8 Hz, respectively. Obviously, the SO₂ concentration was lower than the values in previous reports [8, 9]; and that also happened to the results of previous studies [10, 4]. Besides, a large response at the minimum experimental gas concentration of 2.5 ppm of the Ag@GO sensor is approximately of TLV-TWA and lower than that of TLV-STEL. From the results in Fig. 5a, the sensor's gas sensitivity factor (*S-factor*) in Hz/ppm was determined by the ratio between the frequency shift and the corresponding SO₂ concentration [4]. The *S-factor* was calculated to be 3.28, 6.76, 7.80, 8.27, and 8.43 Hz/ppm at 2.5, 5.0, 7.5, 10.0, and 12.5 ppm, respectively. The highest gas sensitivity of the sensor was 8.98 Hz/ppm at 15 ppm. The ideal sensitivity factor value of the gas sensor is assumed to be constant at all concentrations of a target gas and only depends on the different target gas-types. In contrast, sensitivity factor increases with the increasing of test gas concentration in this case. This phenomenon is caused by the property of the sensing material with the polar gas.

It is possible to determine the amount of SO₂ adsorbed to the saturation state corresponding to each SO₂ exposure cycle at low to high concentrations when applying (1). The adsorbed SO₂ mass results are listed in Table 1 and the relationship between the adsorbed SO₂ mass and the corresponding gas concentration is shown in Fig. 5b. The results indicate that the maximum adsorbed SO₂ mass density is up to $2.38\text{ }\mu\text{g cm}^{-2}$ at 15 ppm and the higher the SO₂ concentration is, the more SO₂ gas molecules adsorbed

by heterogeneous nanomaterial are. As a result, the change in mass on the QCM's active electrode when being exposed to the gas increases with the concentration of the target gas. More specifically, Fig. 5b illustrates a linear increasing relationship between the amount of SO₂ adsorbed by Ag@GO material and the target gas concentration. The linear correlation coefficient of sensor towards SO₂ gas is ($R^2 = 0.999$). Moreover, from the data of calibration line in Fig. 5b, the limit of detection (LOD) was determined by the formula (2): $LOD = 3*S/b$ (where S and b are the standard deviation of sensor noise and the slope of linear fitting, respectively) [19]. In this case, b was 0.176 while S was calculated to be 0.026. According to (2), LOD of Ag@GO sensor was calculated to have a value of 0.44 ppm.

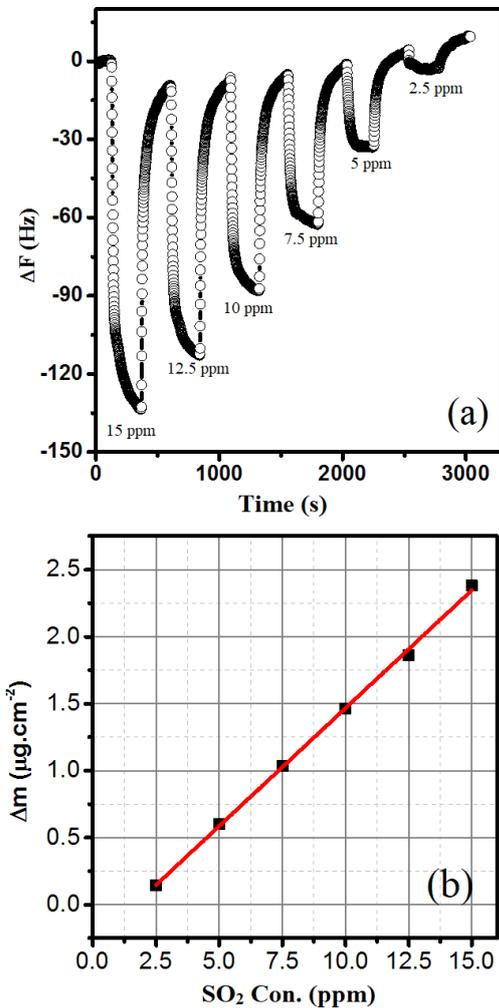


Fig. 5. Gas sensing properties of the Ag@GO coated QCM sensor: (a) the dynamic response-recovery curves and (b) the adsorbed SO₂ mass with various SO₂ concentrations.

In order to investigate the sensor's operating repeatability, a complete 3-cycle response-recovery measurement procedure of the sensor at a concentration of 7.5 ppm was performed and depicted

in Fig. 6. The investigated curve shows similar response-recovery cycles, indicating good repeatability of the sensor. This shape indicates the sensor's good repeatability. The average frequency shift of QCM sensor coated with Ag@GO heterogeneous nanomaterial at 7.5 ppm is -58.2 Hz. This result being equivalent to the measurement result in Fig. 5a demonstrates the stable operation of the sensor at different times.

Table 1: The value of frequency shifts and gas mass adsorbed by Ag@GO heterogeneous nanomaterial and SO₂ gas concentrations.

Con. (ppm)	ΔF (Hz)	Δm ($\mu\text{g cm}^{-2}$)
2.5	-8.2	0.14
5.0	-33.8	0.60
7.5	-58.5	1.03
10	-82.7	1.46
12.5	-105.4	1.86
15	-134.8	2.38

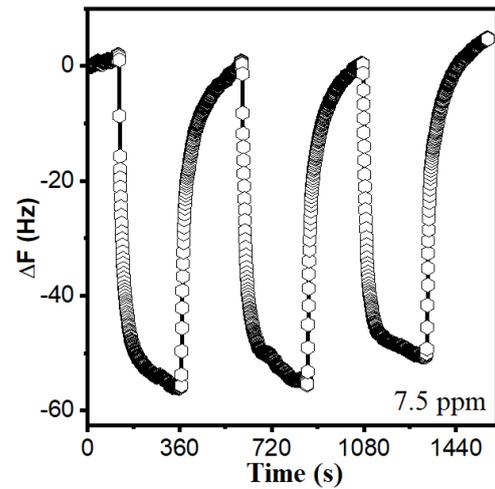


Fig. 6. 3-cycle response-recovery measurement of the Ag@GO - QCM sensor at 7.5 ppm of SO₂ gas

The response and recovery time are one of the most important factors for the reality sensor. The response time is the time to reach 90% of the maximum frequency shifts in the exposure cycle (τ_{res}) while the recovery time is the time need for a sensor to recover 90% of the maximum frequency shifts (τ_{rec}) [20]. Fig. 7 shows the time factors of Ag@GO sensor at 10 ppm (Fig. 7a) and 15 ppm (Fig. 7b). It is seen clear that, the response times in two cases are the same ($\tau_{res} = 95$ s). On other hand, the recovery time of sensor is 100 s at 15 ppm which is slower than recovery time at 10 ppm (90 s). However, the speed of response and recovery were used to accurate evaluate the response and recovery of sensor (v_{res} and v_{rec}). The response rate and recovery rate is determined by the ratio between 90% of the maximum frequency shift and

response/recovery time [4]. The values of ν_{res} and ν_{rec} at 10 ppm/15 ppm were calculated to be 0.684/1.003 and 0.667/0.944 (Hz/s), respectively. It is obvious that the adsorption and desorption speed at 15 ppm are faster than these values at 10 ppm.

The sensor's sensitivity depends primarily on the gas adsorption ability on the surface of Ag@GO heterogeneous nanomaterial. The adsorption between Ag@GO and SO₂ is due to the dipole interaction between the SO₂ polar molecules with functional groups on Ag@GO via hydrogen bonds, with typical bonds on the Ag@GO's surface as oxygen-containing functional groups such as hydroxyl and carbonyl, carboxyl [18]. Fig. 8 shows *S-factor* of QCM coated with GO NSs [18] and Ag@GO heterogeneous nanomaterial at the same concentration. A common characteristic of both sensors is that *S-factor* increases with the increasing concentration of target gas. However, *S-factor* values of Ag@GO sensor are much higher from 8.98 to 13.68 times than GO NSs sensor at each concentration. Moreover, Ag-related heterogeneous nanostructures have been proved to be strong adsorbent to SO₂ [21]. Therefore, the presence and wide dispersion of Ag nanoparticles on GO sheet will lead to higher SO₂ adsorption efficiency at room temperature than that of each individual Ag or GO. Moreover, the results in this work were compared to previous reports summarized in Table.2. It is clearly shown that, Ag@GO heterogeneity is the excellent sensing material at room temperature because *S-factor* of Ag@GO sensor is higher than other references.

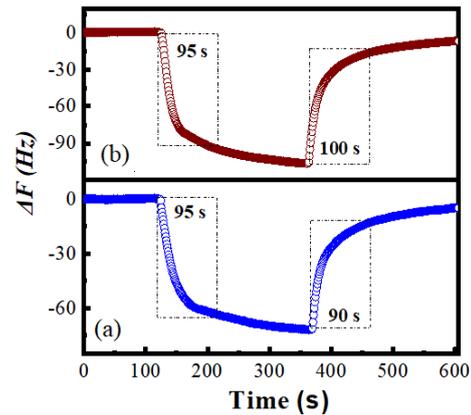


Fig. 7. Response and recovery time of Ag@GO sensor for (a) 10 ppm and (b) 15 ppm

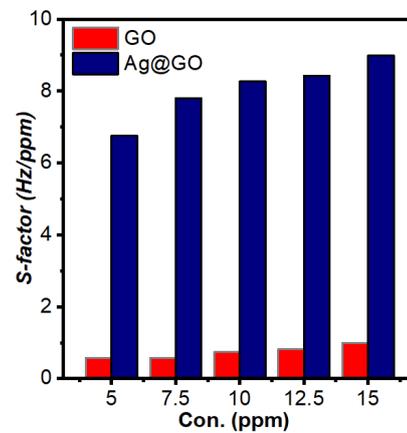


Fig. 8. The comparison between QCM sensors coated with Ag@GO heterogeneous nanomaterial in this work and GO NSs

Table. 2. The results comparison between this work and others.

Sensing material	Con. (ppm)	<i>S-factor</i> (Hz/ppm)	$\Delta m = S\text{-factor} \times \text{Con.} / C_f$ ($\mu\text{g cm}^{-2}$)	LOD (ppm)	τ_{res}/τ_{rec} (s)	References
MWCNT	15	0.413	0.109	2.33	100/90	[10]
GO	15	1.00	0.265	2.50	80/100	[18]
Poly(aniline)		0.11				[9]
Poly(2-methylanilines)	50-250	0.088	-	-	-	
Poly(2-methoxyaniline)		0.19				
		($\Delta f/f$)				[8]
KAUST-7	1 - 500	$-1.6 \cdot 10^{-4}$	-			
KAUST-8		$-1.8 \cdot 10^{-4}$				
$\gamma\text{-Fe}_2\text{O}_3$ NRs	10	2.07	0.366	2.50	65/65	[4]
ZnFe ₂ O ₄ NPs	10	5.20	0.919	1.09	15/15	[22]
Ag@GO heterogeneous	15	8.98	2.379	0.44	95/100	This work

4. Conclusion

In this paper, Ag@GO heterogeneous nanomaterial were successfully synthesized using hydrothermal method. Research focused on using 2D nanomaterial as a stable gas-sensitive/adsorbent layer coated on the active electrode QCM. The results show that Ag@GO heterogeneous nanomaterial were suitable for developing SO₂ gas sensors and exhaust toxic gas adsorbents. Furthermore, the Ag@GO heterogeneous nanomaterial coated the QCM sensor exhibited stable performance, high repeatability, and the highest SO₂ sensitivity reaches 8.98 Hz/ppm. In addition, it can be seen through the response analysis to SO₂ of the fabricated sensor that the Ag@GO heterogeneous nanomaterial had outstanding SO₂ adsorption capacity up to 2.38 μg cm⁻². Especially, Ag@GO heterogeneous nanomaterial absorbed SO₂ gas better than pure GO NSs thank to the enhancement of Ag NPs on GO NSs. These promising results indicate a great potential in the development of emission adsorption material and mass-changing gas sensors at room temperature.

Acknowledgment

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