Nanocomposite of graphene and WO₃ nanowires for carbon monoxide sensors

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ABSTRACT

Due to its harmful nature, carbon monoxide (CO) should be detected at low temperature and in a wide range of CO concentration. A sensor based on WO₃–graphene nanocomposite synthesized by the solvothermal method has been developed. Based on material characterizations, the synthesized monoclinical WO₃ has a nanowire shape. The presence of graphene interestingly promoted the formation of the WO₃ hexagonal structure as a minor phase in the composite. The gas sensor measurements were carried out at three different temperatures, 300 °C, 150 °C, and room temperature. It was found that at 300 °C, the composite with ratio WO₃:graphene 2:1 or WG21 produces a 21.5 response value to 10 ppm of CO, which is higher than the other composites. The response and recovery times of WG21 are 16 and ~4.4 min, respectively. The WG21 nanocomposite was also found to show a good sensitivity in the range concentration of 10–300 ppm.

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1. Introduction

Carbon monoxide (CO) in human blood has more affinity to hemoglobin compared to oxygen, approximately 200 times more. It might cause the protein to be incapable to carry O₂ around human body and can cause hypoxia. The World Health Organization (WHO) stated in 2011 that CO intoxication might be the main cause of intoxication deaths [1]. Depending on CO exposure time, human life could be in danger. Up to two hours of 400 ppm of CO exposure and just 45 min of 800 ppm of CO exposure can cause headache, dizziness, nauseous, loss of judgment [2]. Moreover, the nature of CO that is colorless and odorless making it become a silent killer. Therefore, a highly sensitive and selective CO is necessary to be developed to reduce the life loss due to its toxicity.

Metal-oxide semiconductor-based gas sensors are widely researched due to their low cost, real-time monitoring ability, good response, good portability, and long service life [3,4]. Most metal-oxide semiconductors such as SnO₂, ZnO, TiO₂, In₂O₃, CeO₂, CuO, and WO₃, as the cheapest way to detect CO gas, operate at high temperature between 250 and 350 ºC [5–7]. Most of these oxides have d⁰ and d¹⁰ configurations. TiO₂, V₂O₅, and WO₃, for example, have d⁰ configuration [8]. However, the high operating temperature of the sensor based on metal-oxide leads to high power consumption and lowering both operating temperature and power consumption remains a big challenge [9]. Therefore, an effort to develop low-temperature CO gas sensor is needed.

Tungsten oxide (WO₃) is an n-type semiconductor with a relatively narrow bandgap of 2.4–2.8 eV at room temperature (RT) and it has plenty possibilities for applications such as gas...
The hydrothermal method has very good sensitivity and...
on it so the slurry is deposited on the electrodes and has good contact with the air. The sensor was then dried up at 200 °C for 2 h. The illustration of the gas sensor measurement system can be seen in Figure 1. The gas concentration was controlled by Serinus Cal 3000 with zero air generator that provide N₂ as a mixing gas. The flowrate of the gas was fixed at 0.84 slpm and the change in resistance before and after gas exposure was recorded using PicoTest M3500A digital multimeter.

3. Results and discussion

XRD analysis was deployed to investigate the phase and crystal structure of the WO₃-graphene composite. As seen in Figure 2(i), the WO₃ that has been synthesized by the solvothermal method and calcined at 350 °C, has a monoclinic crystal structure based on JCPDS No. 32-1395. The structure was marked by the peaks at 2θ of 23.08°, 23.71°, 24.46°, 26.57°, 28.76°, 33.24°, 33.68°, and 34.24° which represent the planes of (0 0 2), (2 0 0), (0 2 0), (1 2 0), (1 1 2), (0 2 2), and (2 2 0), respectively. The presence of graphene cannot be observed in the XRD pattern of the composite of WG21 and WG11 as seen in Figure 2(ii) and (iii). The absence of the peak that normally appears at 2θ of 24°, is caused by the small amount of graphene in the composites and by the interfering of (2 0 0) peak of WO₃ that located at the similar region to the (0 0 2) peak of graphene. Interestingly, small peaks at 2θ of 14°, 28.28°, and 36.60° originating from the plans of (1 0 0), (2 0 0), and (111), respectively, start to appear which is originated from the hexagonal structure of WO₃. Those peaks that match well with JCPDS No. 33-1387 are getting stronger in the composite of WG11 indicating the role of graphene as a crystal modifier. As we know, the hexagonal structure of WO₃ normally is promoted by adding a small amount of alkaline metal, hence the hexagonal formation in this case was helped by the carbon atom that acts similar to the alkaline metal. Furthermore, the presence of graphene is observed by the peak appearance at the mentioned angle, in the composite of WG12 as seen in Figure 2(iv). However, the crystallinity of WO₃ is decreased in this composite indicating the existence of very small WO₃ particles that probably decorated the graphene surface. Crystallite sizes calculated by the Scherrer formula show a decrease in size especially in the composite of WG12. The crystallite sizes of WO₃, WG21, WG11, and WG12 are 68, 64, 64, and ~5 nm, respectively. At high portion, graphene can suppress the crystal growth of WO₃.

The effect of graphene on the WO₃ crystal structure was further investigated by Raman spectroscopy. Based on Figure 3(a), there are two patterns in the Raman spectra of WG21 and WG11 that belong to WO₃ and graphene. The peaks in the region of below 1000 cm⁻¹ are typical peaks of WO₃. The spectral of WG21 reveals the presence of both monoclinic and hexagonal phase of WO₃. The peaks at wavenumber of 249, 324, 691 cm⁻¹ are originated from O–W–O deformation and stretching vibration of hexagonal WO₃, respectively. For monoclinic, those vibrations are marked at the wave number of 269, 714, and 804 cm⁻¹ respectively. Moreover, at low concentration of graphene or WG12, the Raman spectral reveals that monoclinic phase of WO₃ is dominant. At high concentration of graphene, the peaks originated form WO₃ do not appear possibly due to the small amount of WO₃. Those results support the XRD result that graphene induces the formation of hexagonal WO₃. In the region above 1000 cm⁻¹, the graphene characteristics are marked at 1581 cm⁻¹ which is known as a graphite (G) band originated from E₂g phonon of sp² carbon, and at 1351 cm⁻¹ which is known as disorder (D) band that originated from defects in the carbon structure. Intensities of the both peaks indicated the quality of the graphene in the composite. Based on Figure 3(a), ratios of D-band to G-band intensity (I_D/I_G) for WG12, WG11, and WG21 are 1.15, 0.74, and 0.78. The ratio tends to decrease...
as the amount of WO₃ increases because a number of WO₃ nanoparticles attach to the graphene surface reducing the lattice defect [49]. Furthermore, the Raman results also show the high stability of graphene after being calcined at 350°C.

FTIR measurement was also carried out to double check the stability of graphene after being calcined at 350°C as seen in Figure 3(b). The broad low band around the wavenumber of 3433 cm⁻¹ is corresponds to –OH stretching vibration from water vapor on the surface of the composites [50]. The small band at 1580 cm⁻¹ is attributed to the asymmetric stretching vibration of COO– that is coming from the graphene and WO₃ interaction [50]. The relatively wide bands at 821 and 711 cm⁻¹ are originate from W–O–W and W–O vibrations, respectively [51,52]. The absence of bands that correspond to W–O–W and W–O vibration in the WG12 sample is caused by the low concentration of WO₃ and the expose dominance of graphene. Based on the results, one can conclude that there is no oxidation process during calcination and the graphene could maintain its structure.

EDS analysis shows that some C is detected in WG21, WG11, and WG12 as seen in Figure 4. In pure WO₃ of course no C can be found. Therefore, it is confirmed that graphene is synthesized as C. Small portion of C can be seen in Figure 4(b) when the graphene portion is quarter amount of WO₃. Moreover the content of graphene increase in Figure 4(c) and (d) that represent WG11 and WG12.

The morphology of each sample was analyzed by SEM characterization. The pure WO₃ was observed to be a nanowire in shape with a diameter in the range of 50–100 nm and length of several micrometers, as seen in Figure 5(a) and (b). Irregular particles exist together with the nanowires structure showing the presence of graphene in the composite of WG21, as seen in Figure 5(c) and (d). The high portion of the oxide is qualitatively seen in the domination of nanowires. Moreover, many irregular bulky particles were observed as the amount of graphene increase in the composite of WG11 and the small number of nanowires still can be found in this composite, as seen in Figure 5(e) and (f). The higher
The concentration of graphene causes the existence of WO$_3$ nanoparticles instead of nanowire as shown by TEM image of WG11 in Figure 6(a, b). The TEM images show the presence of WO$_3$ nanoparticles on the surface of graphene. The bulky particles turn to be a plate-like shape with a thickness of around 500 nm in the composite of WG12 where the graphene is dominant (Figure 5(g) and (h)). It is believed that the plates are consist of graphene and WO$_3$ nanoparticles in the absence of nanowire structure in the SEM images. These results are along with the XRD analysis where at the high portion of graphene or in the composite of WG12, the crystal-lite size decreases significantly to $\sim$5 nm [12,53,54]. Moreover, since the deposition of the nanocomposite was employed by the doctor blade technique, typical thick-film samples were obtained, with an average thickness of each thick-film of 50 $\mu$m.

The response of the sensor is defined by the ratio of the resistance before ($R_a$) and after ($R_g$) CO exposure:

$$\text{Response} = \frac{R_a}{R_g}$$ (1)

As gas sensor materials, responses of all samples to 10 ppm of CO have been tested at three different temperatures that represent high temperature (300 °C), intermediate temperature (150 °C), and RT. As expected, at high temperature, WO$_3$ acts as the main material for CO detection. At this temperature, all samples display n-type sensing characteristics where the resistances decrease soon after they contact with CO. The dynamic responses of WG10, WG21, and WG12 can be seen in Figure 7(a–c). The pure WO$_3$ delivers the response value of 19.5 to 10 ppm of CO. This value increases to 21.5 in the composite of WG21, and reduces abruptly to 1.2 in the composite of WG11 as seen in Figure 8(a). Moreover, the composite of WG12 does not show any response to CO due to the domination of graphene as a CO sensor. Graphene that has zero bandgap and high conductivity, provides more conduction channels in the oxide system and reduces its resistance. The resistances of all samples were recorded to be 10 M$\Omega$, 8.36 M$\Omega$, 31.2 k$\Omega$, and 1.38 k$\Omega$, for WG10, WG21, WG11, and WG12, respectively. It was reported that graphene is semi-metallic and at high temperature, graphene acts similarly to metal, and it is not suitable to be used as a sensing material at high temperature [55,56]. It was proven by no response of graphene to CO at 300 °C and shows small responses at RT and 150 °C that are 1.14 and 1.01. Therefore, the reducing sensor responses in the case of WG11 and zero response in
the case of WG12 are the consequence of WO3 active sites covering by graphene. However, the increase in the response was found in the composite of WG21. In this case, a synergistic effect occurs where the good contact between graphene and the oxide creates a Schottky barrier at the interface and it is very sensitive to the presence of CO [57–59].

At an intermediate temperature of 150°C, we also found that WO3 shows the highest response of 3 to the CO with the same concentration. The presence of graphene reduces the responses to 1.7, 1.02, and 1.01 for WG21, WG11, and WG12 respectively (Figure 8(b)). At this temperature, it is believed that the chemisorption of oxygen molecules starts to occur. However, a synergistic effect seems not to happen and at this temperature, graphene and WO3 are chemically active as the sensing materials. The p-type nature of graphene causes its resistance to increase in its interaction with CO, as opposed to WO3 which has an n-type nature. This phenomenon might cause a low response of all composites. Opposite to what happened at high temperature, graphene has the main role in CO detection at room temperature. It is reflected by the low resistances of all samples with the values of 44.7 and 4.3 kΩ for WG11 and WG 12, respectively. The resistance of WO3 itself could not be recorded due to the limitation of our multimeter that can only measure a resistance up to 120 MΩ. Furthermore, at this temperature, only WG11 and WG12 can deliver responses indicating the domination of graphene as seen in Figure 8(c). In this case, interaction only happens between CO and the surface of graphene. The resistance change occurs due to the redistribution of electrons on the surface caused by CO adsorption and small charge transfer between CO and graphene [60]. The comparison of the CO sensor performance of WG21 with the other nanocomposites and previous reported nanomaterials can be seen in the Table 1 and Table 2. In compared to another reports of RT CO gas sensor, our nanocomposite does not show any response at room temperature. Based on the reported works, the noble metals such as Au, Ag, Pt, and Pd need to be added to help the nanomaterial to detect CO at RT [61–63]. UV irradiation is also reported can improve the oxide performance to detect CO [64].

It is obvious that graphene has a high specific surface area. Its two-dimensional form allows more CO gas to adsorb and provides more gas diffusion paths to access more active sites. These advantages increase the rate of surface reaction and result in shorter response and recovery times relative to the pure WO3. At high temperature, the required time for the WO3 to reach 90% of its final response is 960 s or 16 min. With the presence of graphene in the composite of WG21, the response time decrease...
270 s or 13 min shorter than that of the pure one. The recovery times were also recorded to decrease from 265 to 70 s. Moreover, the response and recovery times of the WG21 versus CO concentration can be seen in Figure 9(d), where either response or recovery time does not have a clear relation with the CO concentration. At the temperature of 150°C, this phenomenon is also observed. The response time of WO3 which is 985 s decrease to 845, 215, and 25 s, in WG21, WG11, and WG12, respectively. While recovery time of WO3 decreases from 1010 to 210 and 55 s in WG21 and WG11, respectively, and rises to 210 s in the composite of WG12. In this case, although the response values are small compare to the pure oxide, the relatively short response times are the advantage of the CO sensor based on the WO3-graphene composite. Furthermore, at room temperature, the response and recovery times of WG11 are 235 and 30 s, respectively, shorter than the response and recovery times of WG12, which are 1025 and 110 s, respectively. The response and recovery times of the nanocomposites are found to be very long and its possibility to suffer from baseline drift due to the releasing of trapped charge or water vapor, will be high. Replacing DC resistance with AC resistance measurement can be a good strategy in the future to shorter the response and recovery times as well as prevent the baseline drift [63].

Since the best performance is delivered by WG21 at 300°C, its gas sensor characteristics were further investigated. Sensitivity of the sensor was measured by varying the CO concentration in the range of 10–300 ppm. As more CO reacted with oxygen species on the composite surface, the response increase as the CO concentration increases to 300 ppm as

| Nanomaterials          | CO concentration (ppm) | T (°C) | Response | Ref.   |
|------------------------|------------------------|--------|----------|--------|
| Ni doped SnO2          | 50 (μL/L)              | 280    | 7.28*    | [65]   |
| Zn doped SnO2          | 50 (μL/L)              | 280    | 5.90*    | [65]   |
| Pt doped SnO2 nanoneedles | 200 (μL/L)          | 250    | 43.7*    | [66]   |
| ZnO nanosheet          | 100                    | 300    | 11.2*    | [67]   |
| In-doped SnO2 nanoparticles | 50                   | 350    | 3.5*     | [68]   |
| Pt/SnO2                | 200                    | 100    | 7*       | [69]   |
| ZnO/3D-RGO             | 1000                   | 200    | 85%b     | [70]   |
| SnO2-graphene          | 30                     | 150    | 88.11%b  | [71]   |
| Au functionalized W52  | 10                     | 31.7   | 1.32*    | [61]   |
| Ag–ZnO/MoS2            | 100                    | RT     | 5.08%b   | [62]   |
| UV-irradiated PANI/TiO2| 13850                  | RT     | 40.3*    | [64]   |
| Pd–In2O3               | 50                     | RT     | 28.4*    | [63]   |
| Pt–In2O3               | 50                     | RT     | 7.2*     | [63]   |
| WO3–graphene           | 10                     | 300    | 21.5*    | This work |

*a S = Ra/Rg.

*b S = Ra/C0 - 100%.

![Figure 9.](image-url)
seen in Figure 9(a). It is also found that the linearity is still fulfilled even when the CO concentration reaches 300 ppm, indicating the wide range detection of the WG21. Furthermore, selectivity of the WG21 was checked by exposing other toxic gases, SO2, NO, CO2, and NO2 with a concentration of 10 ppm at its optimal temperature. As seen in Figure 9(b), the sensor shows good selectivity to CO compare to the other four gases. As known that WO3 has been reported to have very high sensitivity and selectivity to NO2 [72–74]. However, in the presence of graphene, selectivity the oxide to the CO gas improves significantly. This might be due to the presence of oxygen functional groups on the surface of graphene that are very reactive to CO [70,75,76]. This strong interaction is also supported by the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of CO molecules that is allowing direct electron transfer to occur. In order to check its capability to reproduce a similar response, CO response of WG21 at 300 °C was measured every day for five days and the result can be seen in Figure 9(c). The five dynamic response curves display a similar pattern indicating a good stability of the sensor. Aside from the parameters mentioned earlier, humidity effect is also important to be considered as it can reduce the sensing performance. The OH group from water vapor that attaches on the sensor surface can block the CO to reach the surface hence reducing the response [77]. In this work, all measurements were carried out under humidity level in the range of 75–78%. To check the humidity effect, the sensing measurement was conducted under humidity of 40%. At 300 °C, the WG21 resulted in a response of 41 to 10 ppm of CO, almost twice the response under a humidity level of 75% indicating the negative effect of humidity.

Similar to the other oxides, oxygen adsorption is the key in CO detection at elevated temperatures. Under the air atmosphere, the oxygen molecules which are already adsorbed, transform to oxygen ions by taking electrons from the oxide surface. The type of ion species depends on the temperature as summarized in Equations (2)–(4). The chemisorption of oxygen creates a depletion layer on the oxide surface that is associated with the activation energy. The energy can be calculated using Equation (5) [78–80]. Note that k and T are Boltzman constant and temperature respectively. At 300 °C, the activation energy of WO3 is 0.14 eV while the activation energy of WG21 is 0.15 eV. The higher energy is caused by the additional barrier created at the interface of WO3/graphene. The Schottky barrier is generated by Fermi alignment as a consequence of the difference in affinity electron and work function between WO3 and graphene [81]. It was reported that WO3 has affinity electron of 3.33 eV while graphene has work function of 4.7 eV [82]. Fermi alignment occur as electron is transferred from WO3 to graphene generating potential barrier. This barrier is sensitive to the presence of CO gas. During CO exposure, CO transforms to CO2 by reacting with O− and releasing electrons back to the oxide surface (Equation (6)), decreasing the potential barrier as well as the resistance of the composite. Due to the gas sensors operated at 300 °C, the oxygen ion species that are involved in the surface reaction is O2−. In addition, the activation energy of WG11 is 0.007 eV, which is much lower than those of WG10 and WG21. The lower energy of WG11 indicates that the very narrow depletion layer or the main sensing material in the composite is graphene. At 150 °C, the activation energies of WG10 and WG21 are 0.05 and 0.03 eV, respectively, while the energies of WG11 and WG12 are very small indicating the graphene domination. The CO sensing mechanism is depicted in Figure 10. Furthermore, as stated earlier at RT, the main sensing material is graphene. The adsorption of CO on the graphene surface causes electron redistribution resulting in resistance change of the composite.

\[ \text{O}_2 \leftrightarrow \text{O}_2^- \]  \hspace{1cm} (2)
\[ \text{O}_2^- + \text{e}^- \leftrightarrow 2\text{O}^- \]  \hspace{1cm} (3)
\[ \text{O}^- + \text{e}^- \leftrightarrow \text{O}^{2-} \]  \hspace{1cm} (4)
\[ R_e = R_0 e^{-\frac{E_a}{kT}} \]  \hspace{1cm} (5)
\[ \text{CO} + \text{O}^- \rightarrow \text{CO}_2 + \text{e}^- \]  \hspace{1cm} (6)
4. Conclusions

The development of a CO gas sensor based on nanocomposites of WO$_3$ nanowires–graphene was successfully performed using a solvothermal method. As gas sensor materials the composites shows a relatively good responses at 300 and 150 °C. At 300 °C, the presence of graphene in WG21 slightly increases the response from 19.4 to 21.5. This increase in response is caused by the addition of barrier potential at the interface of WO$_3$/graphene. The barriers are associated with the activation energy, where the energy for WG21 is higher than that of WO$_3$. At lower temperatures, graphene was found to not only reduce the sensor’s response but also reduce the response and recovery times of WO$_3$.

Author contributions

For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, B.Y.; methodology, E. and N.L.W.S.; software, M.I.; validation, E. and A.N.; formal analysis, S.Y. and M.I.; investigation, E. and N.L.W.S.; resources, B.Y.; data curation, E.; writing – original draft preparation, E. and N.L.W.S.; writing – review and editing, B.Y.; visualization, N.L.W.S.; supervision, M.I; project administration, E.; funding acquisition, B.Y.

Disclosure statement

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