Electrical and gas sensing properties of TiO$_2$/GO nanocomposites for CO$_2$ sensor application

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Abstract. Titanium dioxide (TiO$_2$) nanostructures were prepared by time varied microwave assisted. The morphology of TiO$_2$ nanostructures was studied by scanning electron microscopy (SEM), X-ray diffraction (XRD). SEM images revealed the agglomeration of TiO$_2$ nanostructures with the size of 20-70 µm. The XRD patterns showed anatase phase of TiO$_2$ with peaks of (101), (004), (200), (105), (211) and (204). The I-V characteristics exhibited the behavior of the ohmic and diode materials. The sensitivity which was measured under CO$_2$ atmosphere at room temperature showed high sensitivity of TiO$_2$/GO composites of 2.55 for 60 seconds.

1. Introduction
The most popular metal oxide semiconductor material is titanium dioxide (TiO$_2$) or titania. TiO$_2$ is n-type semiconductor, and it has two types of crystal structures which consist of anatase and rutile phase. Band gap energy is up to phase of TiO$_2$ (anatase phase of 3.2 eV and rutile phase of 3.0 eV) [1]. TiO$_2$ nanostructures were used in many applications such as photocatalytic or solar cells, lithium ion batteries, and gas sensors [2-4]. The nanostructures of TiO$_2$ can be synthesized by different processes; for example, anodization, thermal evaporation, hydrothermal, microwave-assisted [2, 5-7] etc. These processes can be synthesized various nanostructures of TiO$_2$ such as nanorods, nanotubes, nanowires, agglomerated nanoparticles, thin films, nano-flowers, and nanobelts [2, 8-11].

Graphene is well known for its excellent electrical and thermal conductivity [12, 13]. In addition, nanocomposites of graphene and metal oxides exhibit excellent in hazardous gas and chemical sensing properties [14]. Moreover, graphene can be used in application for Silicon PV Cell by using GO-TiO$_2$ nanocomposites that shows superior absorption peaks more than only TiO$_2$ coated cell [15]. Field emission application from GO/TiO$_2$ and rGO/TiO$_2$ nanocomposites shows turn-on field of 3.3 V/µm and 2.6 V/µm, respectively [12]. Graphene/Polyaniline nanofiber composites were used for supercapacitor electrodes showing 480 F/g at a current density of 0.1 A/g for the highest specific capacitance [16]. Enhancing H$_2$S sensing performances were demonstrated by MoO$_3$/reduced graphene oxide hybrids which have fast response and recovery higher than that of pure α-MoO$_3$ nanorods for operating of low temperature at 110 °C [17].

In this paper, we present the synthesis of TiO$_2$ nanoparticles and TiO$_2$ with graphene oxide (GO) nanocomposites prepared by microwave assisted method and the verification of mixing with and without carbon charcoal (CC) conditions. The application of TiO$_2$/GO nanocomposites CO$_2$ sensing properties was measured under CO$_2$ atmosphere at room temperature for 60 seconds.
2. Experiment

TiO$_2$ nanostructures were prepared by microwave assisted method of pure TiO$_2$ powder and carbon charcoal (CC) materials. First process, the pure TiO$_2$ powder of 0.5 g was put in a crucible. The second process, the pure TiO$_2$ powder of 0.5 g was mixed with carbon charcoal of 0.08 g for comparison the electrical properties of sample materials. Since, carbon charcoal is amorphous phase and very low conductivity. The crucible with the substance of two processes were annealed in a 1000 W-microwave oven for 20 minutes. The sample was removed after temperature of microwave oven cooled down to room temperature. Consequently, morphology of the sample was examined by scanning electron microscopy (SEM) technique (JSM-5410LV, JEOL Ltd., Japan). Crystal structures were investigated by X-ray diffraction (XRD) technique (X’pert MPD, Philips) using Cu K$_\alpha$ radiation with wave length of 1.5406 Å.

To determine electrical properties and sensitivity, TiO$_2$, TiO$_2$/GO, TiO$_2$/CC, and TiO$_2$/CC/GO nanocomposites were prepared as following processes. First, the sample was mixed with Polyethylene Glycol (PEG) and Polyvinyl Alcohol (PVA). Then, the mixture was painted on a microscope slide with dimension of 2.5 cm x 2.5 cm. Next, the samples were heated on a hot plate at temperature of 50 ºC for 10 minutes for drying the sample and making the electrode. After that, the graphene oxide (GO) was dropped on the sample. Finally, the electrical properties of TiO$_2$/GO nanocomposites were studied by I-V characteristics. As a gas sensor, the sensitivity was measured under the CO$_2$ atmosphere at room temperature for 60 seconds.

3. Results and discussions

XRD pattern of the sample, as shown in Fig. 1, confirms that the prepared sample is TiO$_2$ in anatase phase. The peaks occurred at 2 theta of 25.27º, 37.70º, 47.98º, 53.76º, 54.99º, 62.57º, 68.59º, 70.20º, and 74.90º corresponding to (101), (004), (200), (105), (211), (204), (116), (220) and (215), respectively, (JCPDS card NO. 01-071-1167) [18]. The peaks of carbon cannot be observed in XRD pattern due to carbon charcoal was in amorphous phase.

In addition, the crystal size of TiO$_2$ nanostructures can be calculated by using Scherrer equation as shown in equation (1). The crystal size of the sample prepared by using pure TiO$_2$ powder and TiO$_2$ powder mixing carbon charcoal is approximately 44.06 nm and 41.97 nm, respectively. The intensity of the TiO$_2$ peak is higher than TiO$_2$ mixing carbon charcoal peak. Therefore, we can conclude that the crystal arrangement of pure TiO$_2$ nanostructures is more ordered than TiO$_2$/CC nanostructures.
\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

(1)

Fig. 2 shows SEM images with different resolutions of TiO$_2$ nanostructures and TiO$_2$/CC nanostructures. Fig. 2(a) shows agglomeration of the TiO$_2$ nanoparticles [2, 10-11]. The size of agglomerated nanoparticles is approximately 20-70 µm in diameter. Fig. 2(b) shows agglomerated nanoparticles of TiO$_2$/CC. The diameter of agglomerated is the same as in the first case. However, Fig. 2(b) inset represents SEM image with higher resolution. It was observed that the agglomerate consisted of lumps of large carbon charcoal, which expected to be carbon charcoal powder. Since, carbon charcoal was mixed with TiO$_2$ powder in experiment above.

![SEM images](image1.png)  

**Figure 2.** SEM images of TiO$_2$ agglomerated nanoparticles prepared by microwave using times for 20 minutes (a) pure TiO$_2$ powder (b) TiO$_2$ mixed with carbon charcoal.

Subsequently, we studied electrical properties and sensitivity of TiO$_2$ agglomerated nanoparticles and TiO$_2$/GO nanocomposites. The TiO$_2$ and TiO$_2$/CC agglomerated nanoparticles were divided into two parts; the first part, without mixing with graphene oxide and the second part, mixing with graphene oxide.

![I-V and Sensitivity graphs](image2.png)  

**Figure. 3** (a) I-V characteristic of TiO$_2$ nanocomposite measured in air and (b) sensitivity of TiO$_2$ nanocomposite measured under CO$_2$ atmosphere at room temperature.

Fig. 3(a) shows I-V characteristic of TiO$_2$ agglomerated nanoparticles and TiO$_2$/GO nanocomposite. TiO$_2$/GO nanocomposite shows linear relationship indicating the behavior of ohmic material Resistance of TiO$_2$/GO nanocomposite can be calculated by Ohm’s law. As a result, the resistance of TiO$_2$/GO nanocomposite is 3.141 kΩ. However, the green, red and black lines exhibit the behavior of diode material. The resistance of diode material cannot be calculated due to the resistance is inconstant. In
addition, I-V curve characterization reveals that the addition of graphene oxide into TiO$_2$ agglomerated nanoparticles affected electrical properties.

Sensitivity was measured under CO$_2$ atmosphere at room temperature for 60 seconds, and it was demonstrated in Fig. 3(b). The sensitivity value was calculated by the following equation $S = R_{\text{gas}}/R_{\text{air}}$, where $R_{\text{gas}}$, $R_{\text{air}}$ were defined as resistance measured in CO$_2$ and air respectively. The sensitivity of TiO$_2$, TiO$_2$/GO, TiO$_2$/CC and TiO$_2$/CC/GO nanostructures are 1.34, 2.55, 1.29 and 1.29, respectively. Sensitivity of TiO$_2$/GO nanocomposites is higher than that of pure TiO$_2$ as well as TiO$_2$/CC agglomerated nanoparticles [17].

4. Conclusion
The TiO$_2$/GO nanocomposites were successfully synthesized by microwave-assisted method. The XRD patterns revealed anatase phase of TiO$_2$. The crystal size of TiO$_2$ and TiO$_2$/CC agglomerated nanoparticles was 44.06 nm and 41.97 nm, respectively. The morphology of products showed agglomeration of TiO$_2$ nanoparticles with diameter range of 20-70 µm. The I-V curve characteristic demonstrated behavior of ohmic and diode materials. The highest sensitivity of TiO$_2$/GO agglomerated nanoparticles was 2.55.

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