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_2S 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 ºC [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_α 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 ^{o}C 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 25.27^o, 37.70^o, 47.98^o, 53.76^o, 54.99^o, 62.57^o, 68.59^o, 70.20^o, and 74.90^o 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.

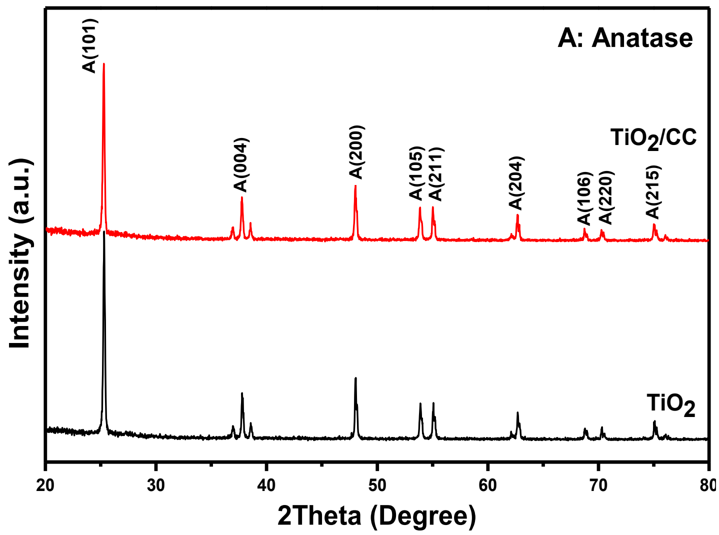

Figure 1. XRD pattern of TiO_2 nanostructures.

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.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

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.

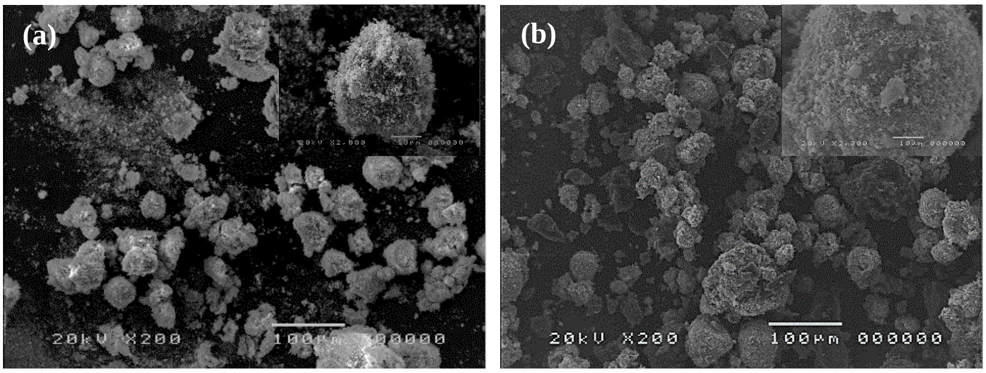

Figure 2. SEM images of TiO_2 agglomerated nanoparticles prepared by microwave using times for 20 minutes (a) pure TiO_2 powder (b) TiO_2 mixed with carbon charcoal.

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.

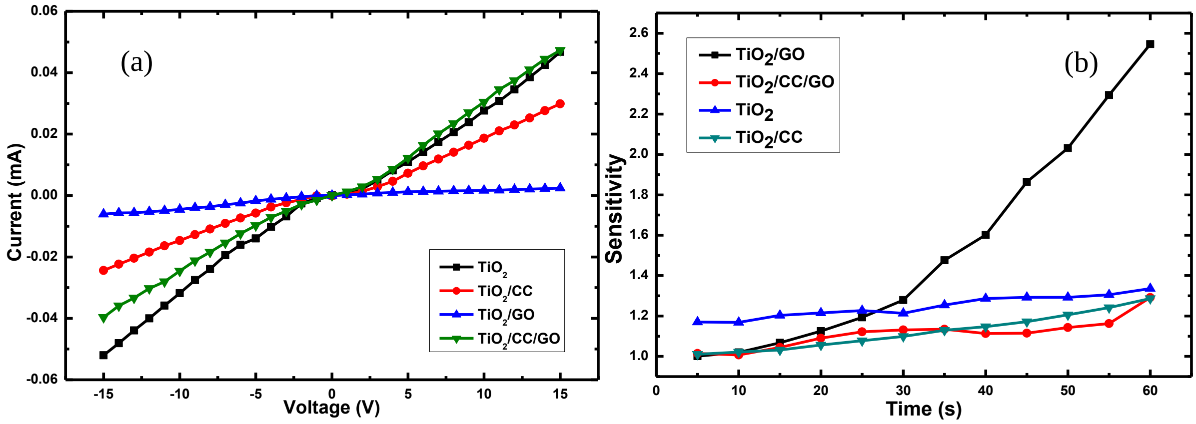

Figure. 3 (a) I-V characteristic of TiO_2 nanocomposite measured in air and (b) sensitivity of TiO_2 nanocomposite measured under CO_2 atmosphere at room temperature.

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 TiO2/GO nanocomposite can be calculated by Ohm's law. As a resul, 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 $S = R_{gas}/R_{air}$, where R_{gas}, R_{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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