Electrical and sensitivity properties of ZnO/TiO$_2$ heterojunction nanocomposites for ammonia gas sensor

P. Chaiyo, C. Makhachan, J. Nutariya, O. Thiabgoh, S. Sumran and S. Pukird*

Department of Physics, Faculty of Science, Ubon Ratchathani University 34190, Thailand
*Email corresponding author: psuparkor27@yahoo.com

Abstract. The ZnO/TiO$_2$ heterojunction nanocomposites were synthesized via a thermal process. The morphology of the samples show TiO$_2$ nanoparticles with range of 50–100 nm in diameter and ZnO nanoparticles with size of upper than 100 nm. The XRD patterns of ZnO/TiO$_2$ nanocomposites indicate ZnO, anatase, and rutile phases. The current - voltage characteristics of ZnO and TiO$_2$ nanoparticles, and ZnO/TiO$_2$ heterojunction nanocomposites show behaviour of ohmic contact materials. The material sensitivity was measured under an ammonia atmosphere for 200 seconds at room temperature. The results showed maximum response of ZnO/TiO$_2$ nanoparticles with 27.30 for 200 seconds.

1. Introduction

Ammonia (NH$_3$) is one of the toxic gases associated with human life. It is widely used as a reactance in chemical industries such as refrigeration system, metal treating operations, paper processing, fertilizer factories, petroleum and mining industries, etc. [1, 2]. Leakage of ammonia gas results in health hazards. An over inhalation of the ammonia leakage can cause an instantaneous death. Therefore, a fast response, high accuracy, and reliable detector is highly demanded for this harmful gas.

Several electronic materials such as metals, metal oxides, conducting polymers, nanostructure ceramics have been employed for the ammonia detectors [1-3]. At present, a metal oxide semiconductor has received a great attention from research communities because it possesses a large surface area to volume ratio, high sensitivity, short response time, and operated at room and high temperatures [2-4]. Typically, the metal oxides are synthesized via many methods for example sol-gel, hydrothermal, chemical vapor deposition (CVD), atomic layer deposition (ALD), electrospinning process, thermal evaporation, and screen-printing technique [5-11]. By these techniques, the structures of the metal oxides materials can be synthesized in a variety of forms such as nanorods, nanowires, nanoparticles, nanotubes, nanobelts, nanosheets, nanospheres, nanoribbons, and nanomaterials heterojunctions [2-3, 12-17]. Besides, the heterojunction structures of composites materials showed an efficient enhancement of the gas detection [18-19].

Recent studies have been explored that ZnO/TiO$_2$ heterojunction sensors are good candidate for gas detection [6, 8-10, 20-24]. Moreover, Sn doped ZnO/TiO$_2$ nanocomposites fabricated by two processes of anodic oxidation and hydrothermal process were used for H$_2$ detection in air atmosphere at
temperatures of 100 – 160 °C. The sensitivity of the ZnO/TiO$_2$ nanocomposites was reported ~ 1.48 [18]. It has been reported that a gas sensor fabricated from ZnO-TiO$_2$ heterojunctions nanofibers responded to an ethanol gas of 20 – 500 ppm [9]. Therefore, ZnO/TiO$_2$ heterojunctions are promising for NH$_3$ detection at room temperature.

The chemical reaction of sensor in air and ammonia gas atmosphere can be described by following equation (1-2), respectively [4, 25-26].

\[
\begin{align*}
O_{ads}^{2-} + 2e^{-} & \leftrightarrow 2O_{ads}^{2-} \\
2NH_3 + 3O_{ads}^{2-} & \rightarrow 2N_2 + 3H_2O + 3e^{-}
\end{align*}
\]

The sensitivity can be calculated via following equation (3)

\[ S = \frac{R_g}{R_a} \]  

Where S is sensitivity, $R_g$ is sensitivity in ammonia atmosphere, and $R_a$ is sensitivity in air atmosphere [25].

In this work, we present the ZnO/TiO$_2$ heterojunction nanocomposites materials. The ZnO/TiO$_2$ heterojunction nanocomposites were prepared by the simply thermal process at a temperature of 900 °C in air atmosphere. Likewise, we report the sensitivity of the TiO$_2$ nanoparticles, the ZnO nanostructures, and the ZnO/TiO$_2$ heterojunction nanocomposites materials for ammonia gas at room temperature.

2. Methods

2.1 Preparation of TiO$_2$ and ZnO nanostructures
Firstly, 0.5 g of TiO$_2$ and 0.5 g of ZnO powder were put in crucible and then placed in the middle of furnace. The furnace was heated up until the temperature reached 900 °C and kept this this temperature for 2 hours under the air atmosphere.

2.2 Preparation of ZnO/TiO$_2$ heterojunction nanocomposites
The TiO$_2$ powder was mixed with ZnO powder at weight ratio of 1:1. After that, they were calcined at the same preparation condition of TiO$_2$ and ZnO powder.

2.3 Characterization
The surface morphology of ZnO/TiO$_2$ heterojunction nanocomposites was investigated by a scanning electron microscopy (SEM, JEOL JSM 5410LV). The crystal structures of samples were characterized by X-ray diffractometer (XRD, Philips – X’Pert MPD) with Cu - K$_\alpha$ radiation and wave length.

2.4 Sensor Fabrication
The samples were mixed with polyethylene glycols (PEG) and polyvinyl alcohol (PVA). Then, the samples were painted on a glass slide with dimension of 2.5 x 2.5 cm$^2$. After that, they were heated on a hot plate at temperatures of 100 °C for 5 minutes. After the fabricated sample cooled down to the room
temperature, they were measured currents – voltages characteristics and ammonia detection under the air atmosphere.

3. Results and discussion

Figure 2 shows the XRD patterns of the synthesis samples. The results exhibit anatase phase of TiO$_2$ in the black line. It is clearly seen that the Anatase phases of the sample appear at plane of (101), (004), (200), (105), (211), (213), (116), (220), and (107), which correspond with the peaks of 25.30, 37.75, 48.00, 53.85, 55.08, 62.67, 68.78, 70.26, and 74.92 (JCPDS NO.1272-21), respectively. In addition, the crystal system of the sample is tetragonal. The blue line pattern indicates hexagonal crystal system of ZnO. The planes of ZnO nanoparticles appear at peaks of 31.51, 34.23, 36.02, 47.28, 56.40, 62.67, 66.14, 67.70, 68.85, and 76.62. These peaks comply with planes of (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004), respectively. However, The XRD pattern of ZnO/TiO$_2$ heterojunction nanocomposites shows very similar to the peak pattern of ZnO and TiO$_2$ structures. For the peaks of TiO$_2$ nanoparticles, they show the rutile and anatase phases.

![Figure 1](image1.png)

**Figure 1.** (a) schematics diagram of sensor preparation (b) and fabricated ammonia sensor.

![Figure 2](image2.png)

**Figure 2.** XRD patterns of TiO$_2$ nanoparticles, ZnO nanoparticles and ZnO/TiO$_2$ heterojunction nanocomposites, respectively.

The surface morphology of the nanoparticles of TiO$_2$ is shown in Figure 3. The obtained nanoparticles are 50 - 100 nm in diameter and uniformly distribute on the surface (see Figure 3 (a)-(b)). In other hands, the sizes of ZnO nanostructures are asymmetric type and they are not uniformly distributed. Figure 3(c)-(d) indicates that the size of ZnO particles are about 50 – 100 µm in diameter which is larger than the
TiO$_2$ nanoparticles. Therefore, the morphology of ZnO/TiO$_2$ heterojunction nanocomposites represents the cluster of small TiO$_2$ nanoparticles and asymmetric particles of ZnO nanostructures (see figure 3(e)-(f)). As can be seen in the figures 4(c)-(f), it seems that the large pellets are consisted of the small size of the crystal and the small size of the grain. The average size of the formed pellets is in the 1-2 µm range. This large surface area is more favourable for gas sensing applications [1, 8]. As a result, the increase of an interfacing area between the sensor and test gas will lead to greater sensitivities.

Figure 4(a) shows linear relations of TiO$_2$ nanoparticles and ZnO/TiO$_2$ heterojunction nanocomposites. Their characteristics present the ohmic types of electronic materials [24, 28]. The TiO$_2$ nanoparticles and ZnO/TiO$_2$ heterojunction nanocomposites resistances are ~1.82 MΩ and 917.43 kΩ, respectively. This infers that the electrical conductivity of ZnO/TiO$_2$ heterojunction nanocomposites is greater than the TiO$_2$ nanoparticles. Because, it has charge transfer between TiO$_2$ and ZnO by way of increasing conductivity of ZnO/TiO$_2$ heterojunction nanocomposites [9, 27-28].

![Figure 3](image1.png)

**Figure 3.** SEM images of (a)–(b) TiO$_2$ nanoparticles, (c)–(d) ZnO nanoparticles, and (e)–(f) ZnO/TiO$_2$ heterojunction nanocomposites

Figure 4(b) shows the sensitivity of TiO$_2$ nanoparticles (red) and ZnO/TiO$_2$ heterojunction nanocomposites (blue) at room temperatures under ammonia atmospheres with gas flow rate of 30 l/min for 200 seconds. The highest sensitivities of TiO$_2$ nanoparticles and ZnO/TiO$_2$ heterojunction
nanocomposites are 13.87 for and 27.30 for 200 seconds, respectively. These suggest that the ZnO/TiO$_2$ heterojunction nanocomposites are faster response and higher sensitivity than the TiO$_2$ nanoparticles.

![Graph A](image1)

![Graph B](image2)

**Figure 4.** (a) I – V characteristics of TiO$_2$ nanoparticles and ZnO/TiO$_2$ heterojunction nanocomposites and (b) Sensitivity of TiO$_2$ nanoparticles and ZnO/TiO$_2$ heterojunction nanocomposites measured at room temperature under ammonia atmosphere.

Moreover, from the results of SEM images, it seems that the size of the crystal and the size of the grain suggest that small crystals stick together into large pellets. Therefore, the surface area was increasing and more touching elements which lead to greater sensitivities [1, 8, 9].

![Diagram A](image3)

![Diagram B](image4)

**Figure 5.** (a) – (b) the schematics showing a gas sensor mechanism of ZnO/TiO$_2$ heterojunction (c) ideal band structures of the ZnO/TiO$_2$ heterojunction materials.
Figure 5 (a) shows gas sensor mechanism in air atmosphere of the ZnO/TiO$_2$ heterojunction nanocomposites materials. The nearly free electron was captured by oxygen near a surface area of the sample. As a result, the electron concentration on the sample surface is low and the depletion layer becomes wider. When the surface area upon exposed to an ammonia gas, the resistance of the ZnO/TiO$_2$ heterojunction nanocomposites become larger. In addition, the ammonia gas reacts with oxygen ions and leave the electron to surface area. Then, the resistance can be increased until the reaction was surcease (see figure 5(b)). This process/mechanism is similar to the finding in ref [9, 28].

Figure 5(c) shows ideal electronic structures of the ZnO/TiO$_2$ heterojunction nanocomposites. Due to ZnO/TiO$_2$ heterojunction nanocomposites is heterojunction composites, they contain a great of free electrons on the surface area. These electrons can be transferred to the surface area. Furthermore, the work functions of TiO$_2$ and ZnO are 4.2 and 5.3 eV, respectively [27]. Consequently, when ZnO/TiO$_2$ heterojunction nanocomposites exposed to air. The oxygen ions capture electrons on TiO$_2$. Therefore, the electron charges will be transferred from TiO$_2$ to ZnO [27, 28].

4. Conclusions
The ZnO nanostructures, TiO$_2$ nanoparticles, and ZnO/TiO$_2$ heterojunction nanocomposites materials were synthesized by a thermal process under air atmosphere. The TiO$_2$ and ZnO cluster of nanoparticles were formed and observed using SEM. The I-V characteristics of ZnO/TiO$_2$ heterojunction nanocomposites showed good ohmic properties. The highest sensitivity of the fabricated sensors is 27.30 for 200 seconds. The synthesized ZnO/TiO$_2$ heterojunction nanocomposites are highly promising for an ammonia gas sensor.

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