The development of gas sensor for carbon monoxide monitoring using nanostructure of Nb–TiO$_2$

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Abstract

The development of titanium dioxide (TiO$_2$) as a gas sensor for combustion and exhaust air pollutants monitoring is strongly dependent on its properties such as thermal stability, grain size and surface area. In this study, nanostructure TiO$_2$ with its thermal stability enhanced by niobium dopant (Nb–TiO$_2$) was synthesized using the water-in-oil (w/o) microemulsion system of $n$-heptane/water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant and was compared with undoped TiO$_2$. It was found that the synthesized powder was of uniform size (14 nm) and high surface area (80 m$^2$/g). Nb-doped TiO$_2$ at a level of 3–5 mole% clearly hinders the anatase to rutile phase transformation and inhibits the grain growth in comparison with pure TiO$_2$. The nanostructure of anatase was maintained even after the powder was fired at 850 °C. The result indicates that sensitivity of CO is significantly increased with an increase of thermal stability of Nb-doped TiO$_2$ in comparison with those of undoped TiO$_2$ and thus is useful for CO sensing studies at high temperatures.

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1. Introduction

The monitoring of toxic and flammable gases has become more important in both domestic and industrial environments. The development in this specific application requires reliable and inexpensive gas sensors. Typically, the metal oxides have been of interest as solid-based semiconductor gas sensors due to their high sensitivity to pollutant gases, small size and low cost. Among metal oxides; TiO$_2$ is the most interesting because of its ability to monitor both indoor and outdoor air quality [1–4,16–17].

The performance of TiO$_2$ as a gas sensor depends on many important factors such as the grain size, size distribution, microstructure, intrinsic properties and crystallographic phase. Typically, TiO$_2$ has three crystallographic phases: brookite, anatase and rutile. The different structures influence the sensing properties. The most sensitive phase for gas sensing is found to be anatase. However, it can easily and irreversibly convert to the rutile phase at about 600 °C. In exhaust air pollutants monitoring, TiO$_2$ as a gas sensor is concerned with the high operating temperature necessary to reach equilibrium between the oxygen in the bulk and that in the gases in the environment. Accordingly, the phase transformation from anatase to rutile can cause a drastic decrease of sensor sensitivity. Beside the effect of phase transformation (thermal stability), sharp increase in sensitivity are expected when the grain size becomes smaller than the space-charge depth. Thus, the maintaining of nanostructure in anatase phase TiO$_2$ film in a high temperature environment is found to be an effective way to increase the sensitivity of gas sensor for exhaust gas sensing applications [4–6,12–15]. In this study, we have focused on synthesis of the nanostructure TiO$_2$ gas sensor with the Nb as a dopant to enhance the thermal stability for CO monitoring. The nanostructure of pure TiO$_2$ and Nb-doped TiO$_2$ were synthesized by a microemulsion system of $n$-heptane/water/NaCl/ sodium bis (2-ethylhexyl) sulfosuccinate (AOT) [8–11]. The physical properties, the thermal stability and microstructure of these TiO$_2$ powders were characterized. The effect of thermal stability on CO gas sensing was studied by measuring the electrical response in laboratory tests.
2. Experimental

2.1. Nanosize TiO₂: preparation and characterization

Pure TiO₂ was prepared by a microemulsion technique according to a procedure described in literature [7]: ten g of the aqueous solution of 0.3 M TiCl₄ was added to 90 g of 6 wt% AOT in n-heptane solution with rapid stirring. After thorough mixing, the solution was equilibrated at 30 °C for 2 hr. For Nb-doped TiO₂, the procedure was slightly modified by adding NbCl₅ in the aqueous phase before mixing. The resulting microemulsion was stable and separated for precipitation, which was carried out by bubbling air through concentrated NH₄OH solution into the microemulsion. The as-synthesized TiO₂ was separated by high-speed centrifugation at 10,000 rpm. Then, it was washed sequentially with n-heptane, twice with ethanol and acetone and finally with water to remove the remaining surfactant from the as-synthesized particles. The as-synthesized TiO₂ was dried and calcined for 5 h at various calcination temperatures. After that, the characterization of the microstructure TiO₂ was carried out by XRD, BET and TEM.

2.2. Microstructural analysis of thick film sensor

After calcination at 460 °C, the TiO₂ powder was formed into a thick-film sensor. Thick-film sensors were fabricated using pastes obtained by adding each powder with an organic vehicle. The pastes were painted on an alumina substrate with an activated Au electrode. The sensor was fired in air at temperatures ranging from 550 to 850 °C and subsequently characterized by XRD. The gas sensing characteristics were examined by fixing the concentration of CO at 1000 ppm and the operating temperature at 550 °C. The electrical responses of the films were observed. The sensitivity was defined as the ratio of \( R_{\text{air}}/R_{\text{gas}} \) where \( R_{\text{air}} \) and \( R_{\text{gas}} \) are the resistance in air and gas exposure, respectively. After gas was applied to the flow system, the oxidizing CO caused a dramatic decrease in resistance of the TiO₂. As a result, a sudden increase in current can be detected. A step response was observed by switching the flow from air to gas and gas to air.

3. Results and discussion

3.1. Nanosize TiO₂ characterization

The effect of calcinations temperature on the nanostructure of TiO₂ was studied at various calcinations temperatures from 450 to 850 °C. TEM observation showed that both Nb-doped and pure TiO₂ powder had uniform morphology in the anatase structure (plane 101) with the characteristic d-spacing of 3.52 Å after the calcinations at 450 °C (Fig. 1(a)–(b)). However, when the temperature was increased to 850 °C, the undoped TiO₂ showed the presence of both anatase and rutile structure, while, Nb-doped TiO₂ was still maintain the anatase structure. The HR-TEM (Fig. 1 (c)) shows the Nb-stabilized anatase structure (plane 101) at 850 °C. The average grain size of pure TiO₂ and Nb-doped TiO₂ was about 20 and 14 nm, respectively.

Fig. 1. TEM image of TiO₂ powder calcined at 450 °C (a), the HR-TEM of anatase structure (plane 101) of pure TiO₂ calcined at 450 °C (b) and 3% Nb-doped TiO₂ calcined at 850 °C (c).
3.2. Microstructure analysis on thick-film TiO₂ sensor

The sensors were prepared from a powder of pure TiO₂ and 3% Nb-doped TiO₂. They were subsequently fired at different temperatures varied from 650 to 950°C. The heat conduction through the alumina substrate during the firing process for sensor preparation may accelerate the phase transformation differently in the calcination process. Thus, the effect of firing temperatures on the phase transformation from anatase to rutile structure of TiO₂ on the alumina substrates was studied again to confirm the crystallographic phases by XRD-thin film mode. The result is shown in Fig. 5. After subtraction of the alumina substrate peak, the percentages of anatase and rutile structures were calculated. The results showed an improvement of thermal stability. The transformation temperature from anatase to rutile structure was increased in the presence of 3% Nb doping. At 850°C, the Nb–TiO₂ was still in pure anatase structure.

4. Gas-sensitivity electrical response of thick film

4.1. The sensor response of TiO₂ on CO

The TiO₂-based films with and without Nb doping were tested as gas sensors at 550°C with 1000 ppm of CO.

The ratio of \( R_{\text{air}}/R_{\text{gas}} \) sensor response was reported as sensitivity.

4.1.1. Sensor response for pure TiO₂

Fig. 6 shows the sensor response to 1000 ppm CO when firing temperatures were varied from 550 to 850°C. The best gas response on CO was obtained when a sensor film was fired at 650°C. This might be due to the presence of nanostructure TiO₂ film with a high percentage of anatase when it was fired at moderate temperatures (650°C). However, at higher temperatures (850°C), the transformation of nanostructure from anatase-to-rutile was accelerated. Moreover, grain growth (150 nm) occurred resulting in a drastic drop in surface area (37 m²/g). When firing at low temperature (550°C), the nanostructure in the anatase phase was retained but the electrical response was low. This is possibly due to the insufficient heat providing to complete the attachment between the film and electrode with a resulting poor signal.

4.1.2. The effect of Nb-doped TiO₂ on sensing properties

For Nb–TiO₂ (Fig. 7), there is obviously an effect because of Nb enhanced thermal stability. The existence of the anatase phase at high temperature results in a better electrical signal of the film on CO. Moreover, the resistance of the film was 10 times lower than that of the pure TiO₂.

Fig. 2. The effect of calcinations temperature on average specific surface area and crystal size of powder. (a) undoped-TiO₂ (b) 3% Nb-TiO₂.

Fig. 3. XRD pattern of pure TiO₂ with various calcination temperatures from 550 to 850°C.

Fig. 4. XRD pattern of Nb-doped TiO₂ at calcination temperature of 850°C.
At 650 °C, the Nb–TiO$_2$ was not in a clear crystal structure. When the firing temperature was increased, the clearer crystal nanostructure in the anatase phase with the average grain size of 10–15 nm and the specific area about 70–80 m$^2$/g was maintained. An increase in thermal stability resulted in a better CO response at 950 °C. Thus, Nb doping is effective in both keeping the nanoparticles size distribution and improving CO response from anatase phase stabilization.

In order to explain clearly the effect of thermal stability, the sensitivity of the film both with and without Nb doping TiO$_2$ with varied calcination temperatures was related to the percentage of anatase structure as shown in Fig. 8. Nb–TiO$_2$ which had the highest percentage of anatase, stabilized at high temperature, shows the best sensitivity at about 2.2. The pure TiO$_2$ which almost turned to the rutile structure at the firing temperature of 850 °C clearly showed a drop in sensitivity. The result clearly indicated improved sensitivity with an increase in thermal stability of a thick film.

A nanostructure with the high thermal stability of niobium doped TiO$_2$ (Nb–TiO$_2$) was synthesized using the water-in-oil (w/o) microemulsion system of n-heptane/water/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant. It was compared with undoped TiO$_2$. It was found that the Nb-doped TiO$_2$ at 3–5 mole% clearly hinders the anatase-to-rutile phase transition and inhibits the grain growth in comparison with pure TiO$_2$. The nanostructure of anatase could be maintained even after the powder was fired at 850 °C. In a CO sensing study, it was found that the sensitivity of CO is significantly increased with an increase of thermal stability of Nb-doped TiO$_2$. By comparison, undoped TiO$_2$ did not behave this way. This shows that the nanostructure of Nb-doped TiO$_2$ is promising for environmental monitoring.
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