Y₂O₃, Pd and Rh₂O₃ added in TiO₂ based sensors materials

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X-ray diffractometry and conductivity data are used to establish the understanding of transformation in titania-based sensor materials. Phase identification of titania in the anatase phase was carried out by X-ray diffractometry. The X-ray diffractometry and conductivity test of the anatase phase were carried out at room temperature. The anatase structure of titania-based materials was understood when it was mixed with yttria, palladium and rhodium (III) oxide. It was observed that the transformation of anatase to rutile phase. However, the presence of palladium and rhodiumoxide in titania-yttria modification had slowed down the transformation of anatase to rutile. Increase of anatase phase increased the conductivity while the rutile phase apparently inhibited the conductivity in the titania-based and titania modified based materials.

Diffractometry, Conductivity, Titania-based, Anatase phase, Rutile phase)

INTRODUCTION

Gas sensors have the function of converting a change in gas concentration into a measured signal. The stimulus can be mechanical, thermal, electromagnetic, or in chemical [1]. Semiconductor gas sensors are one of widely research area based on the ability to temperature while responding to changes in gas composition.

Titania-based is one of the materials that have been investigated for gas sensor materials due to their ability to change to different phases [2]. In titania, the phenomenon of absorption of gas molecules on semiconductor surface efficiently modifies the electrical resistance of material and this is an important property for gas detection. The anatase form of TiO₂ is used for both CO and H₂ gases [3]. The first and most step may be assumed to be the adsorption of CO molecules on the exposed surface, express as below [4]:

\[ \text{TiO}_2 \rightarrow \text{CO}_{\text{ad}}(\text{TiO}_2) \]

This is followed by the ionization of the adsorbed species on the surface, releasing a free electron:

\[ \text{CO}_{\text{ad}}(\text{TiO}_2) \rightarrow \text{CO}^*_{\text{ad}}(\text{TiO}_2) + e^- \]  
(2)

Increase concentration of CO and more charge carriers (e⁻) are generated. Subsequently, the resistance of the sample continues to decrease.

On the other hand,

\[ \text{CO}^*_{\text{ad}}(\text{TiO}_2) \rightarrow \text{CO}_{\text{ad}}(\text{TiO}_2) + \text{H}^+ \]  
(3)

\[ \text{CO}_{\text{ad}}(\text{TiO}_2) \rightarrow \text{CO}(g) \]  
(4)

Thus, CO pressure decreases, resistance of sample increases due to desorption of CO from TiO₂ surface (see eqs. 3 and 4). The understanding of phase transformation from anatase to rutile in TiO₂ and TiO₂ modified materials for gas detection is important. This paper described the transformation of anatase to rutile for different thermal treatment of TiO₂ based materials with mixtures of yttria, palladium and rhodium (III) oxide. X-ray diffractometry (XRD) is a useful tool to characterise the phase transition of anatase to rutile due to the change of crystal structure.
EXPERIMENTAL

Commercial anatase TiO₂ (RDH, purity 99%) in the form of powder was used as starting material. The selective catalyst and dopant materials were added in weight percentage of TiO₂ and coded as in Table 1.

<table>
<thead>
<tr>
<th>Batch coded</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO₂</td>
</tr>
<tr>
<td>TiO₂</td>
<td>100</td>
</tr>
<tr>
<td>T-Rh₂O₃</td>
<td>99</td>
</tr>
<tr>
<td>T-Y₂O₃</td>
<td>90</td>
</tr>
<tr>
<td>T-Y-Rh₂O₃</td>
<td>90</td>
</tr>
<tr>
<td>T-Y-Pd</td>
<td>90</td>
</tr>
<tr>
<td>T-Y-P-Rh₂O₃</td>
<td>90</td>
</tr>
</tbody>
</table>

Note: *N* means number of percentage added into 100% of total TiO₂ + Y₂O₃ mixed composition.

All powder compositions in Table 1 were dried milled for 6 hours. The mixed powders were pelletised into 3mm thickness and 10mm diameter at 2 tons pressure. Pellets were dried in the oven at 100°C for 24 hours. The oven dried pellet samples were fired at temperature 800°C, 900°C, 950°C and 1000°C for 4 hours. The pellet samples are then ready for XRD analysis and conductivity test.

RESULTS AND DISCUSSION

The XRD analysis of the pure titania sample fired at different temperatures for 4 hours is shown in Figure 1. The samples fired at 800°C and 900°C show presence of anatase peak at 2θ=25° while the sample fired at 950°C shows mixed presence of anatase and rutile phase. Lore in her work also found that both anatase and rutile phases in titania coexisted at 950°C for 4hrs [2]. However, sample fired at 1000°C shows only presence of rutile phase at 2θ=27°. To ensure that one is working with the anatase structure, heat treatment for titania based should be below 950°C for 4hrs.

![Figure 1. The XRD spectra of pure titania fired at 800°C, 900°C, 950°C and 1000°C for 4 hours.](image1)

Conductivity Test

The conductivity of pellet samples was measured using Ultrahigh resistance meter model R8340A. 100 volt was supplied for 30s to the pellet and average value of 10 current readings were taken.

X-ray diffractometry

X-ray diffractometer system (XRD) model AXS Bruker was used for each pellet to identify the phase present. The spectra were collected at 2° per minute between 20° to 90° using CuKα radiation at 40 kV voltage and 30mA current. The JCPDS cards in database for each of the respective materials were used for comparison.

![Figure 2. The X-ray powder diffraction spectra of titania based and titania modified based materials fired at 800 °C for 4 hours.](image2)
Figure 3. The X-ray powder diffraction spectra of titania based and titania modified based materials fired at 900°C for 4 hours.

Figure 2 shows strong peak for anatase phase at 2θ=25° in pure titania and modified titania fired at 800°C for 4 hours. The XRD spectrum of T-Y₂O₃ had a peak at 2θ=29° indicating presence of yttrium ion, which was incorporated in the tetragonal crystallographic system of TiO₂. At this firing temperature, no peak at 2θ=27° for rutile phase was present for all samples.

Figure 4. X-ray powder diffraction spectra of titania based and titania modified based materials fired at 950°C for 4hrs.

Figure 3 and Table 2 show the XRD spectra for titania and titania modified samples fired at 900°C for 4 hours. The spectra for sample coded T-Y-Pd, T-Y-Rh₂O₃ and T-Y₂O₃ show presence of mixed anatase and rutile phase. All yttria doped titania modified materials due to yttrium ion presence had influence the crystal lattice deformation and hence lower the anatase to rutile structural transformation temperature to 900°C as indicated in Table 2.

Table 2: Phase transformation from anatase to rutile at different temperatures for TiO₂ and TiO₂ modified samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>800°C</th>
<th>900°C</th>
<th>950°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch coded</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase Peak at 2θ=25°</td>
<td>Strong peak</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Very small</td>
</tr>
<tr>
<td>Rutile Peak at 2θ=27°</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Nil</td>
<td>Strong peak</td>
</tr>
<tr>
<td>T-Rh₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase Peak at 2θ=25°</td>
<td>Strong peak</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Medium peak</td>
</tr>
<tr>
<td>Rutile Peak at 2θ=27°</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Strong peak</td>
<td>Strong peak</td>
</tr>
<tr>
<td>T-Y₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase Peak at 2θ=25°</td>
<td>Strong peak</td>
<td>Small peak</td>
<td>Medium peak</td>
<td>Strong peak</td>
</tr>
<tr>
<td>Rutile Peak at 2θ=27°</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Medium peak</td>
<td>Strong peak</td>
</tr>
<tr>
<td>T-Y-Rh₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase Peak at 2θ=25°</td>
<td>Strong peak</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Medium peak</td>
</tr>
<tr>
<td>Rutile Peak at 2θ=27°</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Medium peak</td>
<td>Strong peak</td>
</tr>
<tr>
<td>T-Y-Pd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase Peak at 2θ=25°</td>
<td>Strong peak</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Strong peak</td>
</tr>
<tr>
<td>Rutile Peak at 2θ=27°</td>
<td>Nil</td>
<td>Strong peak</td>
<td>Strong peak</td>
<td>Strong peak</td>
</tr>
</tbody>
</table>

Table 3: Conductivity measured at room temperature for TiO₂ and TiO₂ modified samples fired at different temperatures.

<table>
<thead>
<tr>
<th>Firing temperature</th>
<th>800°C</th>
<th>900°C</th>
<th>950°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch coded</td>
<td>Conductivity/μA</td>
<td>Conductivity/μA</td>
<td>Conductivity/μA</td>
<td>Conductivity/μA</td>
</tr>
<tr>
<td>TiO₂</td>
<td>12.91 x 10⁻⁴</td>
<td>5.40</td>
<td>0.80</td>
<td>0.54</td>
</tr>
<tr>
<td>T-Rh₂O₃</td>
<td>26.87</td>
<td>14.46</td>
<td>2.85</td>
<td>0.80</td>
</tr>
<tr>
<td>T-Y₂O₃</td>
<td>1.56</td>
<td>0.47</td>
<td>0.22</td>
<td>0.21</td>
</tr>
<tr>
<td>T-Y-Rh₂O₃</td>
<td>2.81</td>
<td>0.48</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>T-Y-Pd</td>
<td>1.89</td>
<td>1.01</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>T-Y-Rh₂O₃</td>
<td>3.23</td>
<td>1.20</td>
<td>0.72</td>
<td>0.39</td>
</tr>
</tbody>
</table>
In contrast, for TiO\(_2\), T-Rh\(_2\)O\(_3\) and T-Y-Pd-Rh\(_2\)O\(_3\) samples at 900 °C for 4 hours only anatase peak at 2\(\theta\)=25° is present and no rutile phase peak at 2\(\theta\)=27°. However, presence of Rh\(_2\)O\(_3\) is seen to slow down the structural transformation to rutile even at 950 °C for 4 hours as shown in Figure 4.

Hishita et al. had reported that the anatase-to-rutile transformation is inhibited by the presence of the rare-earth oxides [5]. Figure 5 shows that at 1000°C for 4 hours all titania based and titania modified base samples are converted to rutile structure. This may be influenced by crystal growth that can be expected during thermal treatment as indicated by Emilija M. Kostic et al. [6].

Table 3 shows the conductivity value reduces as firing temperature increases from 800°C to 1000°C for pure titania and titania modified materials. Increase in deformation of anatase to rutile structure had lower down the conductivity value of all samples. For sensor material, the near insulating property of the materials cannot be used to test the sensitivity and selectivity of the targeted gas species.

**CONCLUSIONS**

1. The XRD spectrum for titania based materials shows that structural transformation from anatase to rutile occurs at firing temperature of 950°C for 4 hours. Based on this result, firing the titania based materials at 900°C for 4 hrs was considered to be the maximum heat treatment at which the transformation could be avoided.

2. Y\(^{3+}\) lowers down the anatase-rutile structural transformation temperature to 900°C for 4 hours in titania and titania modified samples.

3. Rh\(^{3+}\) is seen to slow down the anatase-rutile structural transformation in titania and titania modified samples.

4. The conductivity values of all samples were decreased as firing temperatures increased.

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**REFERENCES**


