SOL-GEL SYNTHESIS AND CHARACTERIZATION OF TiO₂ POWDER

Omer Kaygili 1, Niyazi Bulut 2, Cengiz Tatar 3, Tankut Ates 4, Turan İnce 5

In the present study, TiO₂ powder having the tetragonal crystal without any impurity was easily synthesized by sol-gel method, and its characterization was done by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. The crystallinity degree was found to be of 89.0%. A flaky morphology was observed.

Keywords: Sol-gel synthesis; TiO₂; X-ray diffraction (XRD)

1 Introduction

Titania or titanium dioxide (TiO₂) is a semiconductor material, and the best known crystal forms of TiO₂ are the anatase, rutile and brookite [1, 2]. While the anatase and rutile, which is a thermodynamically stable phase and is the best known polymorph of TiO₂, have the tetragonal crystal system, the brookite has the orthorhombic crystal structure [3]. The anatase and brookite are metastable phases and these are converted the rutile phase after heating [4]. TiO₂ has been synthesized by several techniques, including hydrothermal, solvothermal, sol-gel, direct oxidation, electrodeposition, microwave and, chemical vapor deposition [5-7]. In comparison to the other preparation methods, the sol-gel route has been widely used for synthesizing of TiO₂ since it has some advantages such as low processing temperature, high homogeneity and low preparation cost [8, 9].

The present work focuses on the preparation with a simple sol-gel synthesis and characterization, using the experimental analysis techniques of X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy, of TiO₂ powder.

2 Materials and method

2.1 Synthesis of TiO₂ powder

0.5 M of titanium (IV) butoxide (Ti(OBu₄), Sigma-Aldrich) was dissolved in 100 ml of anhydrous ethanol (C₂H₅OH, Carlo Erba), and then 100 ml of distilled water was added to this solution. The as prepared solution was stirred continuously, and the beginning of gel formation in this mixture was observed in about 10 minutes. Afterwards, this was stirred without heating for 2.5 h in a magnetic stirrer. This was placed in an oven, kept at 60 °C for 24 h, and further dried at 80 °C for 22 h. The as dried was heated in an electric furnace at 1100 °C for 2 h and white TiO₂ powder was obtained.

2.2 Characterization

X-ray diffraction (XRD) data of the as-produced TiO₂ powder was collected on a Rigaku RadB-DMAX II model diffractometer in the 2θ range from 20° to 80° with a step size of 0.02° using Cu Kα radiation with wavelength of 0.15406 nm. A LEO EVO 40xVP scanning electron microscope operated at 20 kV and equipped with an energy dispersive X-ray (EDX, Röntech xflash) was used to observe the morphology and to determine the elemental composition of the as-manufactured TiO₂ sample.

3 Results and Discussion

3.1 XRD analysis

Fig. 1. shows the XRD pattern of the as-prepared TiO₂ sample. The set of the diffraction planes of (110), (101), (200), (111), (210), (220), (002), (310), (301), (112), (311) and (202) was detected. All the peaks on this pattern are in very good harmony with the standard pattern belonging to the rutile phase, having the tetragonal crystal system, of TiO₂ (JCPDS PDF no: 75-1753), and an additional phase was not observed. The observation of the one hundred percent pure rutile phase for the sample produced at the temperature of 1100 °C is in a very good agreement with the result reported by Toyoda et al. [10].

The crystallinity percent (Xc%) value was estimated according to the relation given in elsewhere [11]. This value was calculated to be 89.0%, corresponding to the high crystallinity of the as-prepared TiO₂. Using the full width at half maximum (FWHM, β) and Bragg angle (θ) values belonging to these planes, the average value of the crystallite size (Dₓ) of the sample was calculated by Scherrer equation [12]

\[ D_x = \frac{0.9 \lambda}{\beta \cos \theta} \] (1)

where λ is the X-ray wavelength, which is equal to the value of 0.15406 nm for CuKα radiation. The average value of Dₓ was computed to be 23.21 nm. The crystallite size value was also computed from the slope of Williamson-Hall plot (Fig. 2), using the following equation [13]

\[ \beta \cos \theta = \frac{0.9 \lambda}{D_{wh}} + 4 \varepsilon \sin \theta \] (2)

Where ε is the lattice strain and D_{wh} is the crystallite size. The ε and D_{wh} values are estimated to be 8.521×10⁴ and 27.51 nm, respectively. Both the calculated values of the crystallite size are approximately close to each other, and these values are in a good harmony with Bakri.
et al. [14]. The as-calculated lattice strain may be associated to the high crystallinity [15].

Using the Miller indices \((hkl)\) and distance \((d)\) for two adjacent plane, the lattice parameters \((a=b)\) and \((c)\) and unit cell volume \((V)\) of the sample were calculated according to the following relations belonging to the tetragonal crystal system, respectively [12]:

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2 + c^2} \quad (3)
\]

\[
V = a^2c \quad (4)
\]

The values of the as-calculated parameters are listed in Table 1 and compared to the standard values (JCPDS PDF no: 75-1753), and these values are in very good agreement with the standard values of the data belonging to the rutile phase of TiO\(_2\) given in JCPDS PDF no: 75-1753.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a) (nm)</th>
<th>(c) (nm)</th>
<th>(V) (nm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2) (JCPDS PDF no: 75-1753)</td>
<td>0.45937</td>
<td>0.29587</td>
<td>0.06243</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.45968</td>
<td>0.29614</td>
<td>0.06258</td>
</tr>
</tbody>
</table>

3.2. Morphological and elemental analysis

A flaky morphology without the porosity is observed from scanning electron microscope image taken at an operating voltage of 20 kV and magnification of \(\times20,000\) (Fig. 3). Since any element other than titanium and oxygen is not detected, the EDX data confirm that there is no impurity in the as-prepared TiO\(_2\) sample. Over and above, the EDX result verify the stoichiometry of TiO\(_2\).

4 Conclusions

A high crystalline TiO\(_2\) powder, composed of the rutile phase with the tetragonal crystal system, was synthesized easily via a simple sol-gel technique. Using the well-known Scherrer and Williamson-Hall methods, the crystallite size of the as-manufactured sample was calculated to be 23.21 nm for and 27.51 nm, respectively.
The crystallinity was estimated to be 89.0%, and the higher crystallinity can be related to the lesser lattice strain value. The morphology of TiO$_2$ exhibits the flaky grains, and EDX data show that the as-synthesized sample is the stoichiometric.

5 References


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