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SOL-GEL SYNTHESIS AND CHARACTERIZATION OF TiO_2 POWDER

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Original scientific paper

In the present study, TiO_2 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; TiO_2; X-ray diffraction (XRD)*

1 Introduction

Titania or titanium dioxide (TiO_2) is a semiconductor material, and the best known crystal forms of TiO_2 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 TiO_2, 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]. TiO_2 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 TiO_2 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 TiO_2 powder.

2 Materials and method

2.1 Synthesis of TiO_2 powder

0.5 M of titanium (IV) butoxide ($Ti(OBu)_4$, Sigma-Aldrich) was dissolved in 100 ml of anhydrous ethanol (C_2H_5OH, 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 TiO_2 powder was obtained.

2.2 Characterization

X-ray diffraction (XRD) data of the as-produced TiO_2 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 TiO_2 sample.

3 Results and Discussion

3.1 XRD analysis

Fig. 1. shows the XRD pattern of the as-prepared TiO_2 sample. The set of the diffraction planes of (110), (101), (200), (111), (210), (211), (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 TiO_2 (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 (X*c*%) value was estimated according to the relation given in elsewhere [11]. This value was calculated to be 89.0%, corresponding to the high crsytallinity of the as-prepared TiO_2. 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 (*Ds*) of the sample was calculated by Scherrer equation [12]

$$D_S = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the X-ray wavelength, which is equal to the value of 0.15406 nm for CuKα radiation. The average value of *Ds* 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]

$$\beta \cos\theta = \frac{0.9\lambda}{D_{WH}} + 4\varepsilon \sin\theta \quad (2)$$

Where ε is the lattice strain and D_{WH} is the crystallite size. The ε and D_{WH} values are estimated to be 8.521×10^{-4} 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

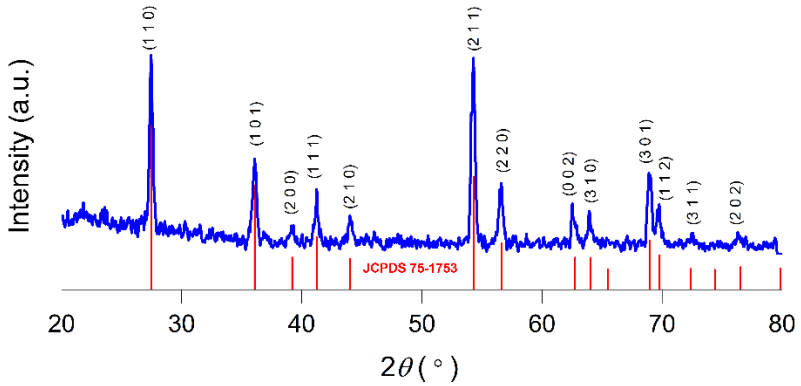

Figure 1. XRD pattern of TiO_2 powder.

et al. [14]. The as-calculated lattice strain may be associated to the high crystallinity [15].

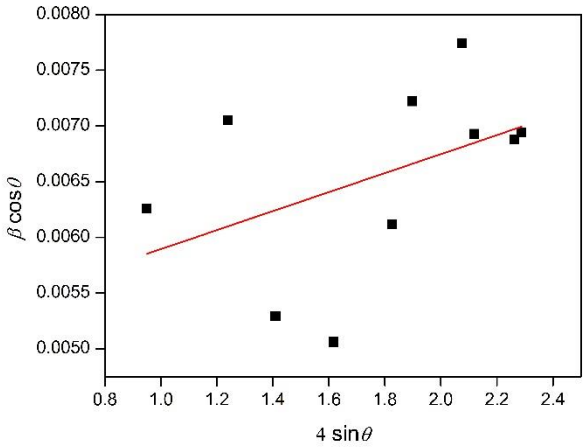

Figure 2. Williamson-Hall plot of TiO_2

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]:

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

$$V = a^2 c \quad (4)$$

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 1. The lattice parameters and unit cell volume of the as-synthesized sample.

Sample	*a* (nm)	*c* (nm)	*V*(nm^3)
TiO_2 (JCPDS PDF no: 75-1753)	0.45937	0.29587	0.06243
TiO_2	0.45968	0.29614	0.06258

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 ×20,000 (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.

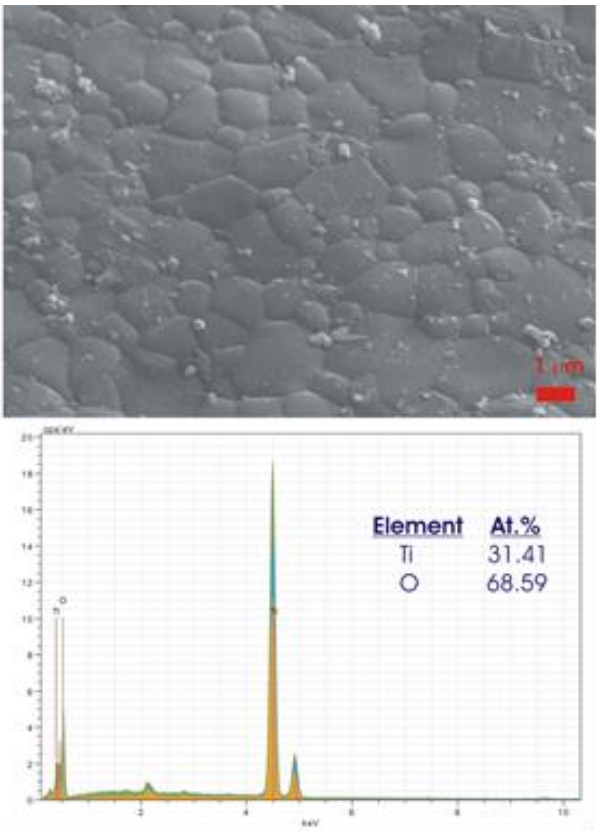

Figure 3. SEM observation and elemental analysis results of the as-produced sample.

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

[1] Chimupala Y, Hyett G, Simpson R, Mitchell R, Douthwaite R, Milne SJ, Brydson RD. Synthesis and characterization of mixed phase anatase TiO_2 and sodium-doped TiO_2 (B) thin films by low pressure chemical vapour deposition (LPCVD). RSC Adv 2014;4:48507-15.

[2] Viana MM, Soares VF, Mohallem NDS. Synthesis and characterization of TiO_2 nanoparticles. Ceram Int 2010;36:2047-53.

[3] Dadkhah M, Salavati-Niasari M, Mir N. Synthesis and characterization of TiO_2 nanoparticles by using new shape controllers and its application in dye sensitized solar cells. J Ind Eng Chem 2014;20:4039-44.

[4] Paunović P, Grozdanov A, Češnovar A, Makreski P, Gentile G, Ranguelov B, Fidančevska E. Characterization of nanoscaled TiO_2 produced by simplified sol–gel method using organometallic precursor. J Eng Mater Technol 2015;137:021003 1-5.

[5] Byranvand MM, Kharat AN, Fatholahi L, Beiranvand ZM. A review on synthesis of nano- TiO_2 via different methods. J Nanostruct 2013;3:1-9.

[6] Li Z, Kawashita M, Doi M. Sol–gel synthesis and characterization of magnetic TiO_2 microspheres. J Ceram Soc Jpn 2010;118:467-73.

[7] Chen X, Mao SS. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. Chem Rev 2007;107:2891-959.

[8] Phonkhokkong T, Thongtem T, Thongtem S, Phuruangrat A, Promnopas W. Synthesis and characterization of TiO_2 nanopowders for fabrication of dye sensitized solar cells. Dig J Nanomater Biostruct 2016;11:81-9.

[9] Sharma A, Karn RK, Pandiyan SK. Synthesis of TiO_2 nanoparticles by sol-gel method and their characterization. J Basic and Appl Eng Res 2014;1:1-5.

[10] Toyoda M, Nanbu Y, Nakazawa Y, Hirano M, Inagaki M. Effect of crystallinity of anatase on photoactivity for methyleneblue decomposition in water. Appl Catal B 2004;49: 227-32.

[11] Kaygili O, Tatar C, Keser S, Bulut N. Preparation and characterization of monetites co-doped with Ni/Al, Ni/Mn and Al/Mn. Mater Lett 2017;201:39-42.

[12] Cullity BD. Elements of X–ray diffraction. Massachusetts: Addison–Wesley Publishing Company;1978.

[13] Mote VD, Purushotham Y, Dole BN. Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. J Theor Appl Phys 2012;6:1-8.

[14] Bakri AS, Sahdan MZ, Adriyanto F, Raship NA, Said NDM, Abdullah SA, Rahim MS. Effect of annealing temperature of titanium dioxide thin films on structural and electrical properties. International Conference on Engineering, Science and Nanotechnology 2016 (ICESNANO 2016), AIP Conference Proceedings 2017;1788:030030.

[15] Hanaor DAH, Sorrell CC. Review of the anatase to rutile phase transformation. J Mater Sci 2011;46:855-74.

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