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The Arabian Journal for Science and Engineering (AJSE)

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THE EFFECT OF SINTERING ON THE PHYSICAL AND OPTICAL PROPERTIES NANO-TiO₂ SYNTHESIZED VIA A MODIFIED HYDROTHERMAL ROUTE

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ABSTRACT: A nano-titanium dioxide (nano-TiO₂) powder, with Zr (0.5-1%) and Nb (0.5-1%) impurities, is fabricated using a modified hydrothermal method, with low-grade mineral precursors. Samples were then sintered at 600°C, 800°C, and 1000°C, then analysed using XRD (crystallite size and phase conversion temperature), SEM (morphology), N₂ Adsorption-Desorption Isotherms (surface area), and UV-Vis-NIR (Absorbance and Optical Transmission), to study the effects of sintering on the structural and optical properties of the synthesized nanopowders. It was discovered that sintering to 1000°C reduces the surface area by 99%, and increases the crystallite size by almost 2000%. Meanwhile, the phase conversion temperature of this sample is 33.3% higher than that reported in literature for 600°C. SEM shows an extensive agglomeration and uneven distribution of nano-TiO₂ particles before sintering. However, the sintered sample shows uniformity in particle size and distribution, and even though it is reduced significantly, agglomeration is still present. The absorbance of the samples is red-shifted towards the visible region (i.e., 380-700nm), with the optical band-gap reduced by 10%, when sintered to 1000°C. The optical transmission of nano-TiO₂ is also reduced by 10% when sintered to 1000°C, due to changes in its microstructure. It is therefore concluded, that sintering nano-TiO₂ improves its structural and optical properties, and paves the way for a multitude of novel applications.

Keywords: nano-TiO₂, hydrothermal, structural properties, optical band-gap, optical transmission

1. Introduction

Titanium dioxide (TiO₂) is a compound that is both familiar, abundant, and has diverse applications. This is due to TiO₂'s novel structural and optical properties. There are various methods of synthesizing TiO₂, with the most common being the sol-gel method [1-2], the hydrothermal and solvothermal methods [3-6], and the more specialized, but seldom used, electrodeposition [7] or sonochemical methods [8].

Recently, extensive research has been conducted on the fabrication and application of TiO₂ in areas, such as photovoltaic devices, electrochromic coatings, and electronic sensors [9]. The flexible nature of TiO₂ allows extensive control and modification of its resulting properties to suit applications as needed. The inclusion of TiO₂ as an integral part of these devices usually has the positive effect of lengthening
process cycles and increasing operating efficiency [10-11]. Nano-TiO₂, due to its size and nature, is also
easily doped with various dopants, having a positive effect on phase transition temperatures, optical
properties, and chemical reactivity.

TiO₂ exists in many forms, making it particularly susceptible to sintering. The common phases of TiO₂ are
anatase (metastable) and rutile (stable). The stabilization of anatase by heating will almost always result
in the formation of rutile. Sintering also inevitably converts TiO₂ from anatase to rutile. Literature indicates
that the phase conversion temperature of anatase to rutile hovers at approximately 600°C, with small
variations depending on the sintering parameters, phases of TiO₂, and the impurities or dopants that are
present.

The objective of this study is to sinter nano-TiO₂ powder (produced via the modified hydrothermal
method), and analyse its effect; such as crystallite size, surface area, morphology, optical absorbance,
and transmittance, on the structural and optical properties. Studying the changes in structural and optical
properties will allow us to predict the behaviour of nano-TiO₂ in extreme temperatures, and recommend it
for potential applications, such as self-cleaning furnaces or hydrophobic coatings on materials operating
under extreme temperatures.

2. Experimental Methods

2.1. Fabrication of nano-TiO₂

The precursor used was a synthetic rutile purchased from Tor Minerals Sdn. Bhd., Perak, Malaysia. The
synthetic rutile was in turn derived from ilmenite, via a hydrometallurgy process. As such, impurities in the
form of Fe, Zr, Nb, and S were present. 100 g of synthetic rutile was fused with 200 g of NaOH pellets at
550°C for 3 hours. The product was then washed and filtered, and the precipitate was collected. The
precipitate was leached using sulphuric acid (2M and 3M) for 4 hours, and the leaching product was
washed and dried in an oven to remove any moisture. Both the 2M and 3M samples were separated and
sintered in a furnace at 600°C, 800°C, and 1000°C, for 2 hours each, producing a total of eight samples for analysis.

2.2. Characterization of nano-TiO₂

The elemental concentrations were determined using Energy Dispersive X-ray Fluorescence (EDXRF). EDXRF provides a rapid and non-destructive method for the analysis of trace and major elements in a sample. All measurements were carried out under vacuum conditions, using a Thermo Electron QuantaX EDXRF spectrometer, with a Cu target, equipped with an electrically-cooled Si(Li) detector. The incident and take-off angles were 20° and 55°, respectively, with a Be window thickness of 7.6 μm. The distance between the sample and the detector was 3.3cm. The concentrations of elements, between Sodium and Uranium, were measured in parts per million (ppm) to the percentage range.

X-Ray Diffraction (XRD) analysis was performed using a PANalytical PW3040/60 X’Pert PRO apparatus. The voltage and anode current used were 40 kV and 30 mA, respectively. The CuKα = 0.15406 nm and the scanning range was set from 20° to 80°.

The samples were also analysed by Nitrogen adsorption-desorption isotherms at 77K using a Quantachrome 1.2 apparatus for its surface area. Prior to each absorption-desorption measurement, the samples were degassed at 373K under P = 0.35509 mm Hg for 24 hours. The specific surface areas were determined using the linearized BET equation at 0 < P/P₀ < 0.30.

The particle's profile and morphology were obtained using an FEI Quanta Scanning Electron Microscope (SEM). The power and working distance was set to 20 kV and 8.1mm, respectively.

Finally, the absorbance and transmission of the samples was determined using a UV-Vis-NIR apparatus, carried out using a Shimadzu UV3600 UV-Vis-NIR Spectrophotometer. The scanning light source had a scanning wavelength of 340nm, and the scan range was set from 200-800nm, at 0.5nm intervals. Two measurement modes were used in this study, namely the reflectance mode and the transmission mode.
The reflectance mode results were converted to absorbance using internal software supplied by Shimadzu, which utilized the Kubelka-Munk equation.

3. Results and Discussion

3.1. EDXRF & XRD Analysis

The process used to produce the nano-TiO₂ in this study, was a slightly modified hydrothermal process. As far as the authors are aware, there is currently no reported work on using a synthetic rutile to produce anatase nano-TiO₂. The hydrothermal process usually involves using expensive and toxic chemicals, such as TTIP, Titanium Butoxide, and Titanium Alkoxide; along with other reagents that need to be carefully mixed in small amounts and autoclaved (hydrothermal treatment) under guarded conditions and controlled environments, to avoid chemical exposure and leakage that might be hazardous [12-13]. The conventional hydrothermal process presents several problems in this work's context, as the hydrothermal treatment involves fusing reagents and precursors at elevated conditions. With a synthetic rutile, this will permanently fuse impurities into the product, potentially contaminating it and eliminating any chances to remove these impurities using physical processes, such as washing, due to the strong bonds formed during the hydrothermal treatment under elevated conditions. Also, the autoclave, being a closed and sealed chamber, disallows visual monitoring of the process, effectively preventing it from being halted before completion. Any potential anomalies that could be spotted visually cannot be rectified until the process has completed, which is clearly too late to do so. The cost of an autoclave is also quite prohibitive, and will inadvertently increase the product's cost. The process and the modification are summarized in Figure 1.

Figure 1: Modified hydrothermal process of nano-TiO₂ synthesis

This process eliminates the use of an autoclave, whilst simultaneously emulating it, thus significantly reducing the time and cost of the whole process. This is achieved by using a rotamantle and a sealed round flask, operating at temperatures below 100°C, aided by constant stirring with a magnetic stirrer.
Processing is done at relatively lower temperatures, it is non-toxic, and manages to produce an almost pure sample of nano-TiO₂ (>95%). The stirring of the solution (kinetics) increases the interaction between the H⁺, SO₄²⁻, and the TiO₂ in the precipitate; thus increasing the leaching rate without elevating the processing parameters to extreme levels.

The samples were then sintered at 600-1000°C, rising at 200°C intervals. According to literature, TiO₂ changes from an anatase to a rutile phase at 600°C. Therefore, sintering at these temperatures will allow us to study the phase changes at different intervals during sintering. Sintering at temperatures of 700°C and 900°C were avoided, because these temperatures are considered intermediate temperatures, where the composition is either dominated by anatase (700°C) or rutile (900°C), with the other phase being a clear minority and insignificant with respect to structural and optical properties. It is surmised that sintering at those two temperatures is not representative of the whole phase conversion process. The specific temperatures of 600°C, 800°C, and 1000°C were chosen to represent three stages i.e., 100% anatase, 50% anatase and 50% rutile, and 100% rutile, respectively.

Samples were analysed using EDXRF and XRD to determine their chemical composition, phase, and crystallite size. This confirms whether the crystallite size is indeed small enough for this TiO₂ to be considered as a nanomaterial, as well as to confirm the existence of impurities within the samples. Table 1 shows the elemental concentration of the nano-TiO₂ produced in this process (in wt %), obtained by EDXRF.

**Table 1: EDXRF analysis of nano-TiO₂**

As observed in Table 1, the presence of Zr and Nb in the sample is quite substantive (~2%) for both 2M and 3M samples; although slightly less so in the 3M sample. This is due to the 3M sulphuric acid being more concentrated, containing more protons (H⁺) and sulphate ions; thus increasing the leaching rate of the system, catalysed by heat (~80°C) and pressure (atmospheric pressure), enabling more TiO₂ to be leached from the precipitate, increasing the overall purity of the product. Fe (126 pm), Nb (146 pm), and
Ti (1.40 pm) are quite similar in atomic radii. Therefore, in limonite-derived synthetic rutile, the Fe and Nb will incorporate themselves into the Ti-O matrix via substitution of the Ti atoms in the Ti-O-Ti bonds. A more rigorous leaching process will render the nano-TiO₂ purer, whilst also incorporating transition metals into the Ti-O matrix. Sulphur is present due to the use of sulphuric acid for the leaching process, and is removable via sintering, as shown in Figures 2 and 3.

**Figure 2:** XRD Diffraction peaks for nano-TiO₂ (2M), where the * notation indicates the Sulfur peak

**Figure 3:** XRD Diffraction peaks for nano-TiO₂ (3M), where the * notation indicate the Sulfur peak

Figures 2 and 3 show the XRD diffraction peaks for both samples. Generally, the samples start in the anatase phase, and gradually convert to rutile. Both samples are at the 50% anatase and rutile stage at 800°C, with full conversion from anatase to rutile at 1000°C. The crystallinity and crystallite size of the samples also increases drastically with sintering. This is indicated by the increasing value of peak intensity, and the lower value of Full Width Half Maximum (FWHM) of each peak, at each increasing sintering temperature [14-16]. Interestingly, both figures show that sintering at 600°C removes the sulphur impurities completely from both samples. Subsequent sintering showed no signs of sulphur.

The conversion of anatase to rutile in the nano-TiO₂ was driven by heat and the recrystallization of the nanoparticles. The process was divided into four stages, starting with the normal anatase phase, followed by the crystal growth of anatase, the coexistence of anatase and the emergence of rutile, and finally, the existence of the rutile phase only; with anatase already fully converted. On getting enough energy from sintering, Ti-O bonds were broken and reoriented [17], even though they stayed in a ditetragonal bipyramidal crystal configuration. When this reorientation occurs, the bond length in the crystal lattice changes (anatase; a = 3.79 Å, c = 9.51 Å, rutile; a = 4.954 Å, c = 2.958 Å). This results in different physical/chemical properties that are inherent to both phases [14]. In this case, the effect of acid concentration is almost non-prevalent. It is only significant at higher concentrations (3M), where it was observed that the conversion of anatase to rutile was 10% slower. This is because the presence of a high concentration of sulphate ions simultaneously inhibits the surface area growth, while simultaneously
encouraging crystal growth in anatase, thus allowing anatase to reach a relatively large crystal size before converting to rutile (compared to the 2M samples), where the sulphate ions are depleted before this could take place. Therefore, the 3M samples seem to have been virtually trapped in the second stage, requiring more energy to move on to the third stage, compared to those samples leached with less concentrated acids. The presence of metallic impurities in the Ti-O matrix caused a slight distortion in the crystal lattice, due to the small difference in atomic radii, which increases lattice strain and inadvertently, its strength. In this case, lattices with impurities require more energy to break and reorient, resulting in a higher phase conversion temperature.

3.2. \( \text{N}_2 \) Adsorption-Desorption Isotherms (BET)

The surface areas of the samples steadily decrease as they are being sintered — this was consistent for both samples. The dispersion of impurities in the sample, and their occupation of substitutional sites in its lattice, contributes to a higher reactivity, due to lattice destabilization [18]. As mentioned previously, the presence of a high number of sulphate ions encourages crystal growth, while simultaneously inhibiting surface area propagation, which curtails its overall reactivity. During sintering, the surface area of all samples is somewhat constant and almost similar. When the crystals merge and form bigger crystals, the surface area per weight decreases, as the surface area is inversely related to crystallite size. This results in sintering producing samples with smaller surface areas.

Figure 4 summarizes the results from the XRD Scherrer calculator for crystallite size (Equation 1) and the \( S_{\text{BET}} \) of both samples.

\[
D = \frac{k \cdot \lambda}{\theta_{1/2} \cos \theta}\]  

(1)

where \( D \) is the crystallite size, \( K^* \) is a constant (ca. 0.9), \( \lambda \) is the X-ray wavelength (1.5418 Å), \( \theta \) is the Bragg angle, and \( \theta_{1/2} \) is the pure diffraction broadening of a peak at half height, due to crystallite dimensions.
Figure 4: Surface area and crystallite size comparison of nano-TiO₂ at different temperatures and concentrations

Although the phases were different, the same behaviour was observed, namely: the crystallite size of nano-TiO₂ increased with sintering [19]. Low leaching concentrations also keep the crystallite sizes small for both phases (i.e., anatase or rutile). This was best demonstrated during the rutile phase, where the size of the 2M samples was almost 10% lower than that of the 3M samples.

Recrystallization of nano-TiO₂ is facilitated by the phase change in the samples. The small, uneven agglomerates of nano-TiO₂ will merge to form bigger and more uniform crystallites when enough energy is provided; in this case, in the form of heat. This is an on-going process during sintering, and will stabilize once the energy for recrystallization is depleted [20].

3.3. SEM

Figures 5 and 6 show the sample's SEM micrographs. Generally, it starts as disarrayed particle agglomerates [21], with very low uniformities. As the sintering temperature is increased, its uniformity is improved. The SEM micrograph supports the theory developed in Sections 3.1 and 3.2. The highly disarrayed and non-uniform crystallites that are present in the samples at 800°C causes the average crystallite size to be small, as it is a combination of small and large crystallites. Small crystallite size equals large surface areas, as the exposed surface from this uneven distribution of size and shapes is huge. However, as the samples go through recrystallization and enter into a two phase (anatase-rutile) state, the particles and crystallites start merging to form more ordered and uniform particles; as seen in Figures 5 and 6 (c) and (d). The almost equal shape, size, and number of particles in the sample per volume, contribute to the generally bigger crystallite size and smaller surface area of the samples at higher sintering temperatures [15].
3.4. UV-Vis-NIR

Figures 7 and 8 show the absorbance spectrum of nano-TiO$_2$ that was leached by 2M and 3M H$_2$SO$_4$, respectively. Both samples show a general absorbance shift towards the visible light region (blue) as the sintering temperature increases. Literature points out that the absorbance of TiO$_2$ is in the UV region (close to 330-350nm). However, in this case, the nano-TiO$_2$ is structurally superior, as shown by its smaller crystallites, higher surface areas, and uniform distribution of particles. This gives way to what is known as the quantum size effect; explained in detail in the works of Liu et al., [14] and Zhang et al., [22]. The larger particles from the sintering allow higher absorption rates of the incident light beyond the UV spectrum (380-450nm), and the absorption spectrum shows a shift towards visible light in both samples [23]. This shift is evident in the sintered sample. Figures 7 and 8 show that sintering increase the visible region shifts of both samples.

Figure 7: Absorbance Spectrum of nano-TiO$_2$ leached by 2M H$_2$SO$_4$

Figure 8: Absorbance Spectrum of nano-TiO$_2$ leached by 3M H$_2$SO$_4$

Absorption rates are affected by a number of factors, such as the light scattering and opacity of the samples. In this case, light scattering might be exacerbated by the presence of metallic impurities, which may serve to scatter incident light and lower the overall absorbance. However, this is not evident, as it is speculated that the incorporation and elimination of these impurities (in the case of sulphur) prevents it from seriously affecting the absorbance; as it acts in tandem with other Ti-O-Ti matrices in the overall structure.
The derivation of the absorbance spectrum allows us to determine the optical band-gap of the samples by extrapolating the linear region of the most prominent absorbance peak in the spectrum, and incorporating this wavelength into Equation 2, to solve $E_g$ [24].

$$E_g = \frac{1240}{\lambda}$$

(2)

**Table 2: Summary of the optical band-gap of the samples**

Corresponding to the absorption spectrum, the optical band-gap of the samples generally decreases as the samples are sintered [23]. This pattern is generally similar for both samples, although the 3M leached sample has a smaller optical band-gap than its 2M counterpart, due to its crystallites being smaller, thus allowing less absorbance and light scattering. Figure 9 summarizes the relationship between optical band-gap and sintering temperature, in the scope of this work.

**Figure 9: The relationship between optical bandgap ($E_g$) and sintering temperature in nano-TiO$_2$**

**Figure 10: Optical Transmission Spectrum of the 2M-leached sample**

**Figure 11: Optical Transmission Spectrum of the 3M-leached sample**

Figures 10 and 11 shows the optical transmission spectrum of the 2M and 3M samples, respectively. Similar to absorbance, optical transmission is also affected by the change in structural properties [13]. The transmission of the samples decreases as the sintering temperature increases, due to the increase in crystallite size, the decrease in specific surface area, and potential light scattering. Figure 10 shows that the transmission is lowest in the UV-Vis region (350-450nm) for all samples, but starts to increase to ~85% at 550nm, and maximizes at 90% at 700nm, for the unsintered sample. The sample sintered at 1000°C showed almost no transmittance at the UV region; at 550nm, its transmittance was 40%; with it peaking at 60% at 700nm. The same behavior was observed for the 3M samples shown in Figure 11. However, the overall transmittance of the 2M samples was slightly better (by 10% overall) due to their smaller crystallite size and larger specific surface area. Low transmissions were recorded in the region of
350-450nm for both samples, because the absorption in this region was the strongest (as shown in Figures 7 and 8), and absorbs the majority of incident light that passes through it, allowing little to pass through. Structural properties, such as crystallite size, packing factor, and uniformity, also play a major role in determining the optical properties. As seen in Figures 5 and 6, sintering increases the crystallite size and packing factor of both samples, allowing sintered samples to actually absorb more incident light, and only allow a little through. Interestingly, the samples sintered at 600°C are the best, because their particles are just beginning to organize into a more uniform pattern, the agglomeration of the unsintered sample is broken, and the particles are loosely packed because of this. The unsintered samples are still amorphous; therefore, packing factors and crystallinity, which play a major role in transmittance and absorbance, inferior greatly with the 600°C sintered sample. As observed in Figures 10 and 11, as the sintering temperatures are increased, optical transmission decreases to a noticeable level. In this case, the 2M leached samples showed better overall optical transmission than their 3M leached counterparts, due to smaller crystallites, loose packing and uniformity, and lower agglomeration.

4. Conclusions

Nano-TiO₂ was prepared via a modified hydrothermal method, using a low cost, non-toxic precursor. The nano-TiO₂ was sintered at 600°C, 800°C, and 1000°C, and characterized using EDXRF, XRD, BET, SEM, and UV-Vis-NIR. Nano-TiO₂ underwent three changes during sintering i.e., phase changes from anatase to rutile at 800°C, its surface area decreased, and its crystallite size and crystallinity increased. Its optical band-gap decreased with increasing sintering temperatures, while optical transmission was recorded at close to 90% at the 500nm regions for the 600°C sintered samples. It is therefore concluded that the TiO₂ nanosized particles, and the subtle presence of impurities, improved the structural and optical properties; even though the nanoparticles reaction did not radically depart from the expected behaviour.
Acknowledgement

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