Original Research Article

X-ray Crystallographic Derived Diffraction Pattern Profiling of Polymorph-TiO_2 for Pigment and Acrylic Paint

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ABSTRACT

At a very low temperature high crystalline TiO_2 best-fitted strain anatase was synthesized by peptization which was the prime focus of this study. Unresolved parameters were investigated by X-ray diffraction (XRD) techniques employed for lattice parameters, crystal size, lattice volume, strain, crystal structure, d-spacing and weight fraction. 54.40 % anatase, 29.1 % brookite and 16.5 % rutile were found by WPPF (Rietveld's refinement) and lattice volume of anatase 137.150, brookite 267.079 and rutile 62.901 Å³ as well the crystal strain 0.307, 0.45 and 0.28 % of anatase, brookite and rutile polymorph-TiO_2 respectively. The average crystallite size was 7.39 nm which confirmed the formation of nanocrystal-$TiO_{2.}$ The strain of the individual polymorphs of TiO_2 show best-fitted used for the pigment and acrylic paint.

Keywords: Acrylic Paint, Anatase, Brookite, Pigment, Rutile

1. Introduction

Pablo Picasso turned forty in 1921, and not long after, an industrial process for making titanium white pigment was created and made public [1]. He has been employing titanium white as a photocatalyst in his work [2], which might seriously harm his reputation and he wasn't the only one [1]. Apart from its application in paintings [3-6], titanium white has also been included in plastic art pieces and photographic paper (resin-coated prints), resulting in issues with deterioration [7, 8]. An established photocatalyst is titanium dioxide. A series of reactions may result in the creation of radicals when titanium dioxide absorbs UV light. These free radicals can damage nearby pigment, which can lead to an organic medium breakdown and embrittlement, gloss loss, or chalking. The colour may also change when dyestuffs, pigments, or colourants are used [9–11]. Pigments made of titanium dioxide have been appropriately used to give a variety of materials opacity or whiteness. Various sectors, including plastics, paints, paper, and inks, can utilize them [12]. Because of its high refractive index and capacity to absorb UV radiation, TiO_2 has several remarkable properties that have earned it an exceptional reputation among other white pigments. These advantages include effective light scattering and product durability. Additionally, because it is non-toxic, there is less risk to safety and health, making it suitable for use in a variety of applications [13].TiO_2 nanoparticles exhibit distinct optical behaviours in comparison to traditional TiO_2 pigments. TiO_2 nanoparticles' optical characteristics are explained by the Rayleigh theory of light scattering. Small particles more effectively scatter light at shorter wavelengths, according to this theory. Additionally, the anatase form of TiO_2 nanoparticles' photocatalytic activity has been used to create a variety of materials with the self-cleaning feature [14]. The industry has paid a lot of attention lately to self-cleaning coatings that use photocatalytic titanium dioxide nanoparticles. TiO_2 nanoparticles have a strong oxidation capacity that can be utilized to eradicate dirt stains or kill bacteria that have adhered to walls. Moreover, when such a coating is put on external surfaces, the super-hydrophilic nature of dirt and stains can make it simple for water or rainfall to wash them away [15, 16]. Because of their incredibly high surface area to particle size ratio, nanoparticles also have a strong potential to agglomerate. Thus, dispersing the nanoparticles without agglomerating in the organic binders is essential for creating an appropriate TiO_2-modified paint. The surfaces of the TiO_2 nanoparticles are coated with sufficient precipitated inorganic compounds, such as SiO_2 and Al_2O_3, to enhance their dispersion and decrease their photoactivity [16]. Commercially obtainable three TiO_2 nanoparticles have been used as additions in varying quantities to white acrylic water-based paint to study how this improves the paint's ability to clean itself. The primary focus of our study is the ultrafine highly crystalline polymorph-TiO_2, which we synthesized in the forms of rutile, brookite, and anatase.

2. Materials and Method

Titanium isopropoxide (TTIP), Ethanol, Nitric acid, Isopropyl alcohol (IP), and De-ionized water are purchased from Sigma-Aldrich. The precursor solution TTIP and IP was mixed with a 1: 3 ratio (v/v) and stirred for 10.00 minutes. On another 500.00 ml beaker add 250.00 ml DI water and maintain pH for 2.0 to 2.5. The prepared two solutions were mixed with and followed the 400.00 rpm and 65 ◦C for 17-18h peptization of the gel was formed. After the peptization, the gel volume decreases to 50.0 cm^3. The final suspension was washed with ethanol with centrifuged at 8000.00 rpm several times. The precipitated dried at oven 60.0 $^{\circ}C$ a white fine powder was obtained. After preparing the sample at 9.0 hours the crystallographic measurement techniques were employed.

3. Characterization

The Smart-Lab SE, a versatile X-ray Diffractometer manufactured by Rigaku in Japan, was used to observe X-ray diffraction patterns. The instrument was equipped with a 40 KV x 50 mA (2.00 kW) source, 10.00mm CBO-BB optics, and a K_β filter made of Ni $_{(28).}$ In this case, the procedure was executed with a step size of 0.001^0 (speed of 05^0/min) and a HyPix-400 (HPAD-1D) detector operating in standard mode, collecting 10^6/pixel rate data. The crystallographic structure and lattice parameters of a material are ascertained by subjecting the material to irradiation with incoming X-rays and subsequently measuring the diffraction angles and intensities of the X-rays that exit the material. The analysis was conducted on the powdered material at a temperature of 25℃, which corresponds to room temperature. X-ray diffraction is commonly used to determine the crystal structure of polymorph-TiO_2. The Debye-Scherrer formula has been utilized to determine the size of crystallites by X-ray diffraction examination.

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where, D = Crystal size, λ = Wavelength of the X-ray (λ=0.1541 nm), β = Full width at half maximum and θ = Diffraction angle [17].

Bragg`s law has been applied for the determination of the d-spacing values (inter-planar distance between atoms)

$$d = \frac{\lambda}{2sin\theta}$$

Table 1 is utilized for the listing of the crystal size and d-spacing values that are determined. The quantitative analysis of the manufactured powder-TiO_2 was determined using the WPPF technique (Whole powder pattern fitting method) given in Table 6.

4. Result and Discussion

The X-ray crystallographic diffractogram revealed three prominent diffractions at 2ϴ angles of 25.38, 37.26, and 48.22, with corresponding intensities of 3927, 554, and 927 counts per second (cps). On the other hand, two minor diffractions were also observed at 2ϴ= 30.65 and 54.5 with intensities of 227 and 801 cps. The main three diffractions 25.38, 37.26 and 48.22 were responsible for anatase-TiO_2[ICDD Card No # 01-083-5914]and another two diffractions 30.65 and 54.5 were responsible for brookite and rutile-TiO_2 polymorphs respectively which as shown in Fig 1.

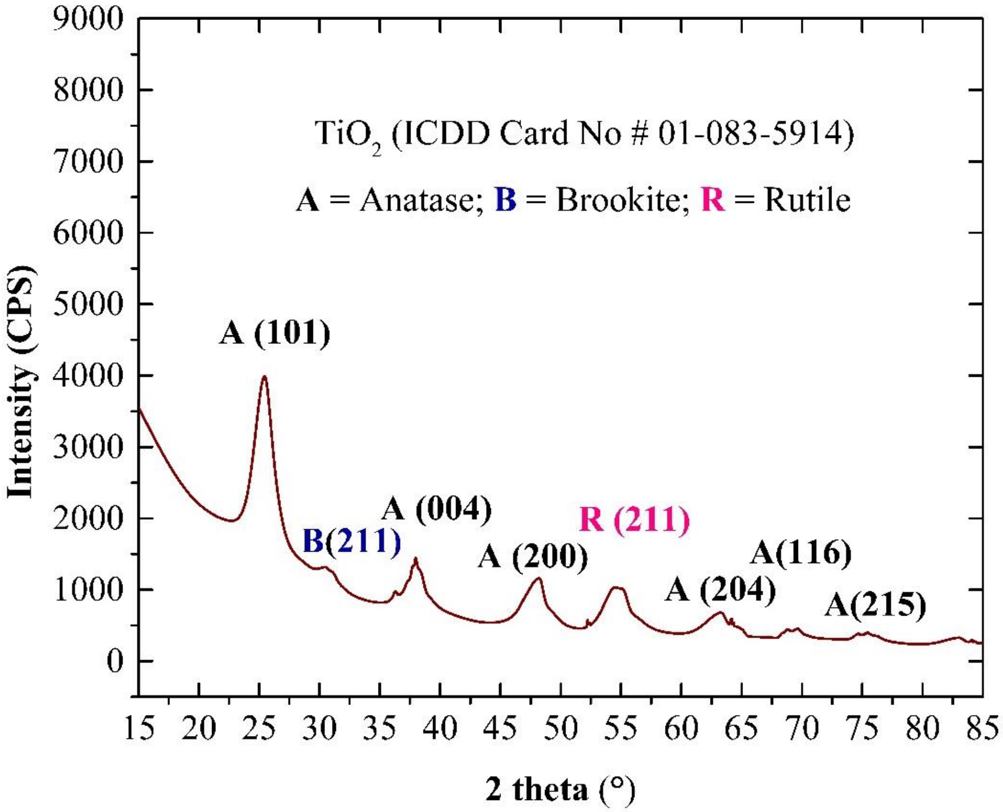

Fig. 1. X-ray diffractogram of TiO$_2$

The minor diffraction was found at 2ϴ= 63.41, 69.43 and 75.73 with intensity of 457, 76 and 58 cps which is also responsible for the prominent anatase [ICDD Card No # 01-083-5914].

Table 1. The calculation of the grain size of TiO$_2$

Diffraction angle (2ϴ)	Theta (ϴ)	(hkl)	FWHM (radians)	Size of the crystallite (D)nm	d-spacing (d), (nm)
25.38	12.69	(1 0 1)	1.453	5.87	0.35056
37.26	18.63	(0 0 4)	0.79	11.20	0.24110
48.22	24.11	(2 0 0)	1.792	5.08	0.18858

Table 1, shows that the three main diffractions were observed at 25.38, 37.26 and 48.22 with the prominent respective Miller indices (101), (004) and (200). The crystal size was determined by the Debye-Scherrer formula with three respective diffractions such as 5.87, 11.20 and 5.08 nm. The calculated average crystallite size was 7.39nm which confirmed the formation of nanocrystal-TiO_2 that shows an outstanding dispersion on paint medium[12]. The interplanar distance (d-spacing) was also calculated by the Bragg formula of the main three intense diffractions. The calculated distance at 25.38, 37.26 and 48.22 were 0.35056, 0.24110 and 0.18858 nm. This d-spacing exhibits the uniformity of the nanocrystal-TiO_2[17].

Table 2. Peak profiling of TiO_2 by diffraction angle

Diffraction angle (2Ɵ)	Theta (Ɵ)	1000× $Sin^2Ɵ$	Reflection	Remarks
25.38	12.69	48.25	(1 0 1)	$1^2 + 0^2 + 1^2 = 2$
37.26	18.63	102.05	(0 0 4)	$0^2 + 0^2 + 4^2 = 16$
48.22	24.11	166.863	(2 0 0)	$2^2 + 0^2 + 0^2 = 4$

Table 2, exhibits the peak profiling of the TiO_2 by diffraction position. Three significant values of the peak profiling were 48.25, 102.50 and 166.83 observed at the 2Ɵ= 25.38, 37.26 and 48.22. The peak profiling and remarks value interval also ensured the particles were uniformly distributed onto the plane into the crystal system [17].

Table 3. Peak profiling of TiO_2 by inter-planner (d-spacing) distance

Diffraction angle (2Ɵ)	Inter-planner distance (d), (Å)	$1000/d^2$	Reflection	Remarks
25.38	3.5056	81.37	(1 0 1)	$1^2 + 0^2 + 1^2 = 2$
37.26	2.4110	172.05	(0 0 4)	$0^2 + 0^2 + 4^2 = 16$
48.22	1.8858	281.21	(2 0 0)	$2^2 + 0^2 + 0^2 = 4$

Table 3, exhibits the peak profiling of the TiO_2 by d-spacing. The peak profiling was 81.37, 172.05 and 281.21 observed at the 2Ɵ= 25.38, 37.26 and 48.22 values with respective d-spacing 3.5056, 2.4110 and 1.8858 Å. Three significant interval values from peak profiling ensure that the crystals are well-growth onto the plane for their uniform distribution as well as remarks value.

Table 4. An analysis of the experimental (Exp.) and standard (Std.) diffraction data is being conducted for comparison.

Diffraction angle (2Θ)		Inter-planer distance (d) (Å)		Lattice parameters of Std.
(Exp.)	(Std.)	(Exp.)	(Std.)	Space Group: I41/amd (141) a=b= 3.7845 Å c= 9.5111 Å; α=β=γ=90.0°; c/a: 2.513, Volume= 136.22 Å^3. [ICDD Card No # 01-083-5914]
25.38	25.307	3.5056	3.516360	
37.26	37.804	2.4110	2.377780	
48.22	48.042	1.8858	1.892250	

Table 4 displays the comparison between experimental data and standard data from ICDD Card No # 01-083-5914. The standard diffractions were detected at 25.307, 37.804, and 48.042, whereas the synthetic TiO2 diffraction was seen at 2Θ= 25.38, 37.26, and 48.22, which closely matches the standard data.The ICDD bilographic shown as Space Group: I41/amd (141)a=b= 3.7845 Å c= 9.5111 Å; α=β=γ=90.0°; c/a: 2.513, Volume= 136.22 Å.Alternatively, the d-spacing values of the standard data were observed at 3.516360, 2.377780 and 1.892250 Å which is also similar to the synthesized TiO_2 d-spacing 3.5056, 2.4110 and 1.8858 Å.

Table 5. Calculation of Percentage of Crystallinity

2Θ (Exp.)	Norm. I. (%) (Exp.)	Percent of Crystallinity (%)	2Θ (Std.)	Norm. I. (%) (Std.)	Percent of Crystallinity (%)
25.38	100.00	53.80	25.307	100.00	70.20
37.26	14.00		37.804	18.00	
48.22	72.00		48.042	24.50	

Table 5, represents the normalized intensity (I.) of the synthesized TiO_2 and ICDD standard. The I. calculated values of synthesized TiO_2 were 100.00, 14.0 and 72.00 at the diffraction position

2ϴ= 25.38, 37.26 and 48.22. So, the crystallinity was observed at 53.80% whereas the ICDD standard shows the crystallinity at 70.20% confirming that it the highly ordered [17] in a three-dimensional lattice.

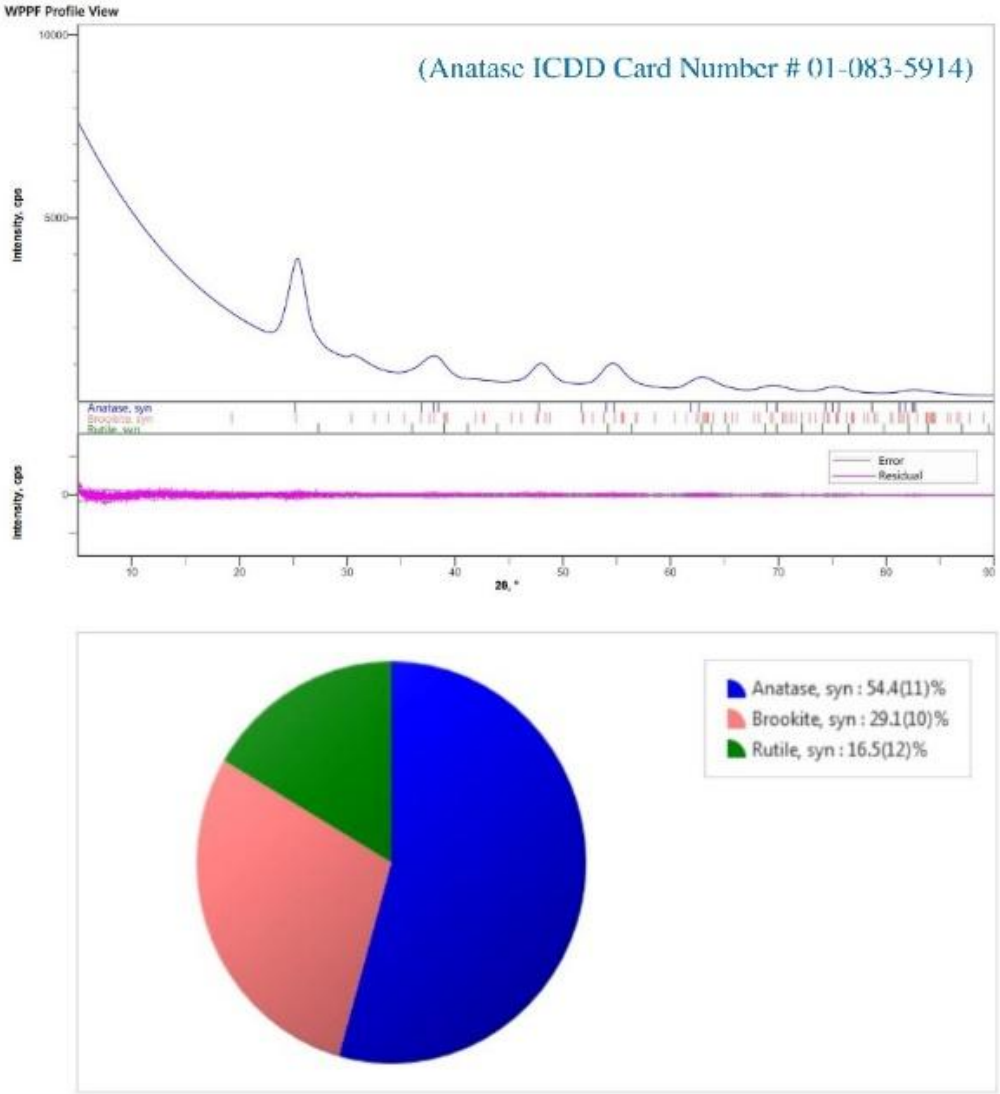

Fig. 2. Quantitative analysis of Polymorph-TiO_2 by the WPPF (Whole powder pattern fitting) method

Fig. 2. Shows the phase percentage (%) of the crystalline polymorphs of TiO_2 that is determined by the WPPF method. The calculated phase percentage observed that 54.40 % anatase, 29.1 % brookite and 16.5 % rutile were found at the pattern fitting condition Rwp, 9.84 %, Rp 7.01 %, S 0.4092, χ^2 0.1674.

Table 6. Rietveld’s refinement of the polymorph-TiO_2

Rwp (%)	Rp (%) and S	Weight fraction, Wt (%)	Lattice volume (Å³)	Strain (%)	Lattice parameters
			Anatase		
9.84	7.01 0.4092	54.40	137.150	0.307	α=β=γ=90.0° a=b=3.8056Å, c=9.470Å
			Brookite		
9.84	7.01 0.4092	29.1	267.079	0.45	α=β=γ=90.0° a=9.186 Å b=5.500Å, c=5.287Å
			Rutile		
9.84	7.01 0.4092	16.50	62.901	0.28	α=β=γ=90.0° a=b=4.613 Å, c=2.956 Å

Table 6. shows the Rietveld refinement of the polymorph-TiO_2 at the same pattern-fitting condition whereas the calculated lattice volume of anatase 137.150, brookite 267.079 and rutile 62.901 Å³ as well as the crystal strain 0.307, 0.45 and 0.28 % of anatase, brookite and rutile polymorph respectively. The strain ensured that the stability of crystalline polymorph-TiO_2 was suitable for the paint medium. The crystal lattice parameters are also calculated by Rietveld refinement, whereas anatase α=β=γ=90.0°, a=b=3.8056Å, c=9.470 Å; brookite α=β=γ=90.0°, a=9.186 Å b=5.500Å, c=5.287Å; rutile α=β=γ=90.0°, a=b=4.613 Å, c=2.956 Å; for its fitted data confirmed the uniformity of the crystal are best suitable to the UV and other radiation that was various prominent application for the pigment and acrylic paint.

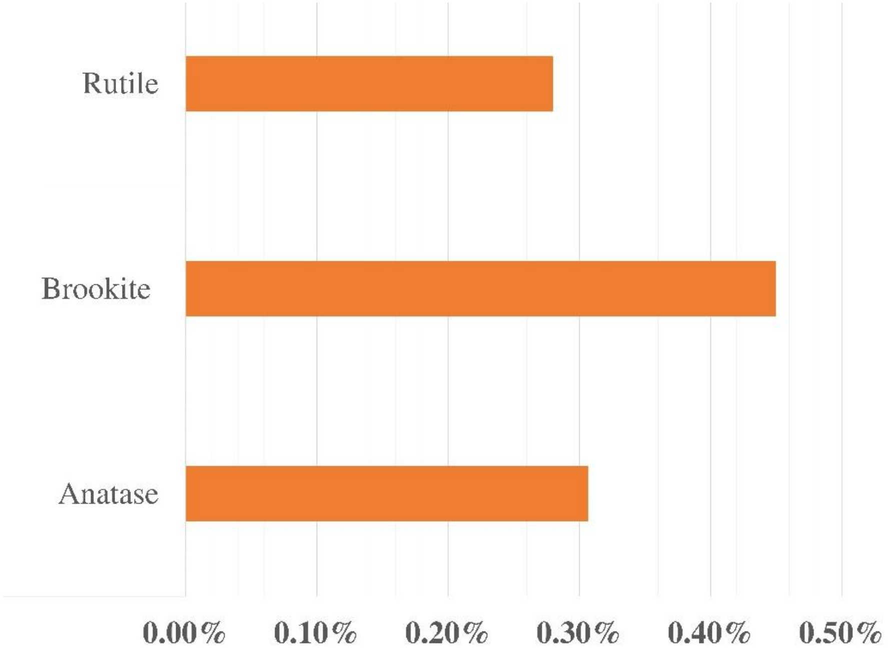

Fig. 3. Strain curve of polymorph-TiO_2

Fig. 3. strain curve shows that the anatase strain curve is more stable than brookite cure as well as rutile. So, the anatase strain is preferred to the paint for its antimicrobial and light scattering properties as well as self-cleaning for the rutile polymorph strain.The application of TiO2 coating is possible on various surfaces including the surface of indoor and outdoor buildings, metallic objects, wooden frames, and domestic and professional instruments[18]. Rutile and anatase are the two polymorphs of TiO2 but the rutile form of TiO_2 cannot boost implemented photocatalytic activity [18,19]. On the contrary, the anatase form can enhance the photocatalytic activity when mixed with paint [20,21]. The addition of TiO_2 into the paint can modify the paint performance traits including peeling, wake retention, cracking, flaking, and muckraking [22]. Moreover, TiO_2 can enhance opacity and brightness and it can improve the durability of the paint [23].TiO_2 is a widely known pigment because of its identical properties (including inert, stable, less costly, and non-toxic) [24]. As an exceptional UV light absorber, TiO_2 defenses from damage that occurs due to UV radiation [23,25]. Because of the identical features of TiO_2, medicinal products with very minute concentrations of pigment can reveal appealing shades and

distinctive characteristics [24]. For tinting a variety of products in the cosmetics and pharmaceutical industries, TiO_2 is extensively used as a pigment [24,26]. Across this industry, TiO_2 is employed to produce several products including lotions, shampoos, sunscreens, toothpaste, and so on [27]. The prepared sample might be used for the pigments as well as for acrylic paint.

Conclusion

High crystalline 54.40% TiO_2 best-fitted strain anatase was synthesized at a very low temperature 60.0 $^{\circ}$C. Exhaustive parameters were investigated by X-ray diffraction (XRD) techniques employed for lattice parameters, crystal size, lattice volume, strain and weight fraction. 54.40 % anatase, 29.1 % brookite and 16.5 % rutile were found by WPPF and lattice volume of anatase 137.150, brookite 267.079 and rutile 62.901 $Å^3$ as well the crystal strain 0.307, 0.45 and 0.28 % of anatase, brookite and rutile polymorph respectively. The strain of the individual polymorphs of TiO_2 show best-fitted used for the pigment and acrylic paint. The average crystallite size was 7.39 nm which confirmed the formation of nanocrystal-TiO_2. For the outstanding significant properties of the TiO_2 it could be very useful materials for the paint, wallpaper, colour-bank and pigment industry.

Data Availability

Data is available on request

Reference

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