



Influence of pH on the Formulation of TiO₂ Nanocrystalline Powders

Abdel-Hamid El-Shear, Ali Basuni*, Mohsen Mosaad

Physics Department, Faculty of Science, Kafrelsheikh University, Kafrelsheikh, Egypt

Email address:

elshaer@sci.kfs.edu.eg (Abdel-Hamid El-Shear), alibasuni98@yahoo.com (A. Basuni), mohsenmoh2003@yahoo.com (M. Mosaad)

*Corresponding author

To cite this article:

Abdel-Hamid El-Shear, Ali Basuni, Mohsen Mosaad. Influence of pH on the Formulation of TiO₂ Nanocrystalline Powders. *American Journal of Materials Synthesis and Processing*. Vol. 2, No. 4, 2017, pp. 51-55. doi: 10.11648/j.ajmsp.20170204.11

Received: June 21, 2017; Accepted: July 6, 2017; Published: July 31, 2017

Abstract: TiO₂ nanoparticles were prepared by Sol-Gel method at different pH values (4, 3.5, 3, 2.5, and 2). All samples were heated at 500°C for 18 h. The optical, morphological, and structural properties of the samples have been investigated using XRD, SEM, and UV-vis spectrophotometer techniques. The results indicated the formation of TiO₂ nanoparticles with pure Anatase phase at pH= 4 and 3.5, while further decreasing of pH, the Rutile phase start to appear intensively compare to Anatase phase. For pH=3, the ratio Rutile phase to Anatase phase was found to be around 76%.

Keywords: Titanium Dioxide (TiO₂), Anatase Rutile Transformation, XRD, SEM, UV-Vis Spectrophotometer

1. Introduction

Titanium dioxide nanoparticles (TiO₂) is a material with excellent optical and electrical characteristics, and it has many potential applications in photocatalysis and dye-sensitized solar cells (DSCs) [1-5].

Titania nanoparticles are typically synthesized in three different crystalline structures; anatase, rutile, or brookite [6], the first two types are mainly used as industrial materials [7]. Anatase and rutile structures are based on distorted TiO₆ octahedra, and due to slightly different bonding lengths and angles between titanium and oxygen atoms, they have different space groups and cell parameters. Anatase has I 41/amd space group with cell parameters of a=3.784 and c=9.515, whereas rutile has P42/mnm space group with cell parameters of a=4.5936 and c=2.9587 [8, 9]. Both structures are tetragonal. Brookite, on the other hand, has a more complicated orthorhombic structure with Pbca space group and cell parameters of a=9.184, b=5.447, and c=5.145 [8, 10]. Brookite has been considered to be brittle, and generally it is less studied than the other two crystal structures, even experimentally. Although brookite is usually considered to be industrially uninteresting there are, however, some reasonable recent studies on brookite nanorods as highly active photocatalysts [11]. The experimental band gap of anatase TiO₂ is 3.2 eV, and the band gap is indirect. Rutile is

thermodynamicly the most stable form of TiO₂, and it can withstand high temperatures, whereas anatase and brookite are converted to rutile when heated. Rutile has quite high measured melting point of 1840 ± 10°C [12]. Rutile has experimentally measured direct band gap of 3.14 eV, where anatase has band gap of 3.55 eV [13].

In case of all the crystalline forms, each Ti⁴⁺ ions are surrounded by an irregular octahedron of oxide ions. In the rutile structure each octahedron is in contact with 10 neighbour octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in anatase structure each octahedron is in contact with eight neighbours (4 sharing an edge and four sharing a corner). The octahedral linkage in brookite is such that three edges are shared per octahedron [14].

Anatase (A) phase is less stable and undergoes transition into rutile (R) phase because of its low density. This transformation takes place between temperatures 450 and 1200°C [15]. The transformation is dependent on several parameters such as initial particle size, initial phase, dopant concentration, reaction atmosphere and calcination temperature, etc. [16-19]. The control of A to R phase transitions, which is an irreversible process, is necessary for the performance of this material in many applications such as sensors, photocatalysis, pigments and electronics [20]. From the mechanism of A to R transformation, it seems that phase transformation is a nucleation and growth process [21, 22].

In this work, an effect of pH level on AR transformation will be studied. Pure and mixed phase of TiO₂ nanoparticles have been successfully grown by controlling in level of pH value during growth processing.

2. Experimental

Titanium (i v) iso-propoxide [C₁₂H₂₈O₄Ti, purity 97%, Sigma-Aldrich] and 2-propanol [(CH₃)₂CHOH] (purity 99% Sigma-Aldrich) are mixed with each other in volume ratio 1:4 respectively, then the resulted mixture is stirred for one hour. Another mixture of deionized water and 2-propanol with volume ratio 1:1 is added, the mixture is stirred for one hour more. pH value of the solution was adjusted at 2, 2.5, 3, 3.5, and 4 by adding HCl acid (concentration 98%, Sigma-Aldrich). The final solution is stirred for one hour at room temperature. Final mixture was put in water path at 80°C to evaporate any liquid in mixture. A resulted white powder TiO₂ is heated for all samples with different pH values at 500°C for 18 h.

XRD measurements of all samples carried out with Shimadzu diffractometer using CuK α radiation with a

wavelength of 0.154 nm. The XRD data were collected at scan step of 0.02°, scan speed of 8.0°/min, 40 kV, and 30 mA. Absorption spectrums of our samples have been measured by UV-vis spectrophotometer model (JASCO V-630). All morphology images have been taken by SEM system model (JEOL JSM-651OLV).

3. Results and Discussion

Figure 1 shows XRD patterns of TiO₂ samples that were prepared at different pH values and were annealed at 500°C. It is noticed from figure 1 that samples prepared at pH value 4 and 3.5, have the diffraction peaks appeared at 2 θ values 25.3°, 38.11°, 48°, 53.59°, 55.24°, 62.9°, 68.86°, 75.07°, corresponds to the crystal planes of (101), (004), (200), (105), (211), (204), (220), and (215) respectively. This indicates to a formation of anatase phase of TiO₂. This result has a good agreement with the literature report (Akarsuet al. [23]). The location of the peaks was compared to literature values and the presence of anatase Titanium dioxide particles was confirmed.

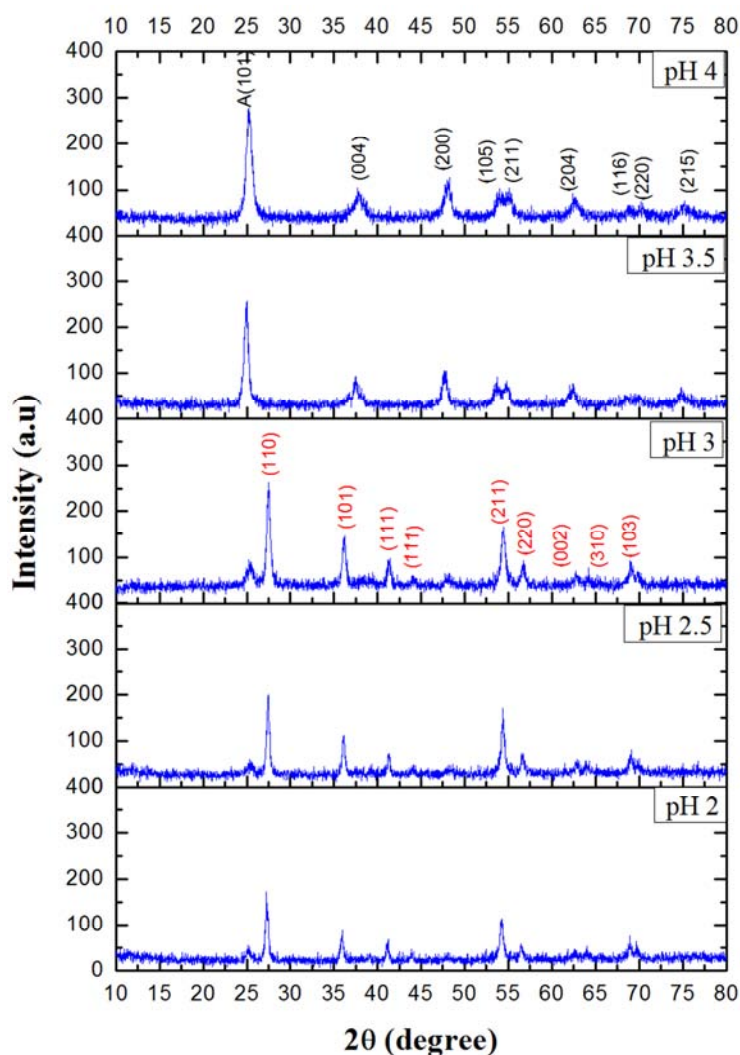


Figure 1. XRD patterns of TiO₂ nanoparticles prepared at different pH values.

By decreasing pH value to 3, 2.5, and 2 we noticed that an intensity of the peak located at $2\theta = 25.3^\circ$, has been decreased to very lower intensities. The diffraction peaks at 2θ values 27.5° , 36.2° , 41.3° , 44.17° , 48° , 54.44° , 56.67° , 64.19° , 69° correspond to the crystal planes of (110), (101), (111), (210), (200), (211), (220), (310), (103) respectively indicating the formation of rutile phases of TiO_2 nanoparticles. The diffraction peaks at 2θ with 25.3° , 63° correspond to the crystal planes of (101), (002) respectively refer to anatase phase of TiO_2 nanoparticles. The presence of anatase and rutile phases of TiO_2 was confirmed by comparing with (JCPDS standard files #21-1272 and #21-1276), respectively [24]. From these results, it is clear that Anatase Rutile Transformation (ART) occurs at pH value lower than 3.5. This result has good agreement with previous reports on ART of TiO_2 nanoparticles [25]. From the mechanism of A to R transformation, it seems that phase transformation is a nucleation and growth process [22, 26]. Also it is stated that in the synthesis of TiO_2 by various methods, the initial crystalline TiO_2 phase formed is generally anatase [27, 28]. From a structural perspective, this could be due to the greater ease of the short-range ordered TiO_6 octahedra in arranging into long-range ordered anatase structure owing to the less-constrained molecular construction of anatase relative to rutile [29].

The relative weight fractions of anatase phase, W_A , and rutile phase, W_R , are calculated using the relative intensity of the (1 0 1) peak of anatase and the (1 1 0) peak of rutile and the relationship $W_R = 1 / (1 + 0.8I_A/I_R)$ and $W_A = 1 / (1 + 1.26I_R/I_A)$ as used by Spurr and Myers [30]. These calculations have been done for mixed phase samples (e. g. pH value equal 3, 2.5, and 2). Results are shown in table 1.

Table 1. Fraction weights of Rutile and anatase (W_R and W_A respectively) at different pH value.

pH value	Phase structure	W_R	W_A
4	Pure anatase	-	-
3.5	Pure anatase	-	-
3	Mixed phase	0.768	0.2305
2.5	Mixed phase	0.799	0.1995
2	Mixed phase	0.7997	0.199

From table 1, a sample that prepared at pH 3 has mixed phase where 76.8% of sample have rutile phase structure while only 23.05% of sample have anatase phase. By decreasing pH value to lower levels, a percentage of rutile phase more increase while a percentage of anatase phase more decrease. It is reported that ART is irreversible process [25]. Furthermore, it is reported frequently that a mixed anatase/rutile or anatase/brookite/rutile phase composition is advantageous for photocatalytic and optoelectronic applications owing to improved charge carrier separation [31-33].

The crystal size for all samples was calculated by using Scherrer equation. Results are shown in figure 2. It is clear that the average crystal size of TiO_2 nanoparticles is decreased with increasing in pH value during synthesis

method. This occurs because of the changing in phase of TiO_2 nanoparticles.

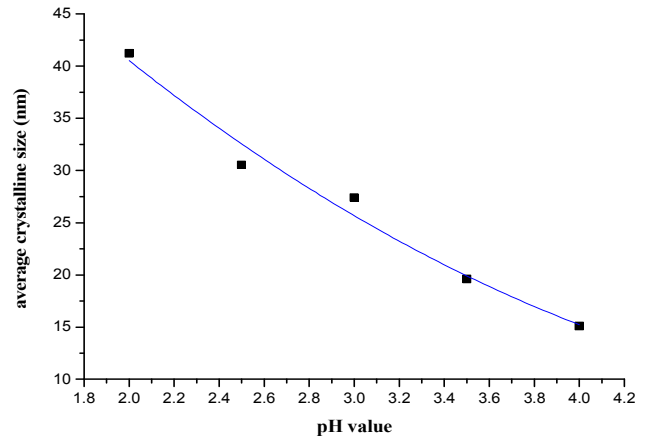


Figure 2. A relation between average crystal size of TiO_2 nanoparticles and pH value.

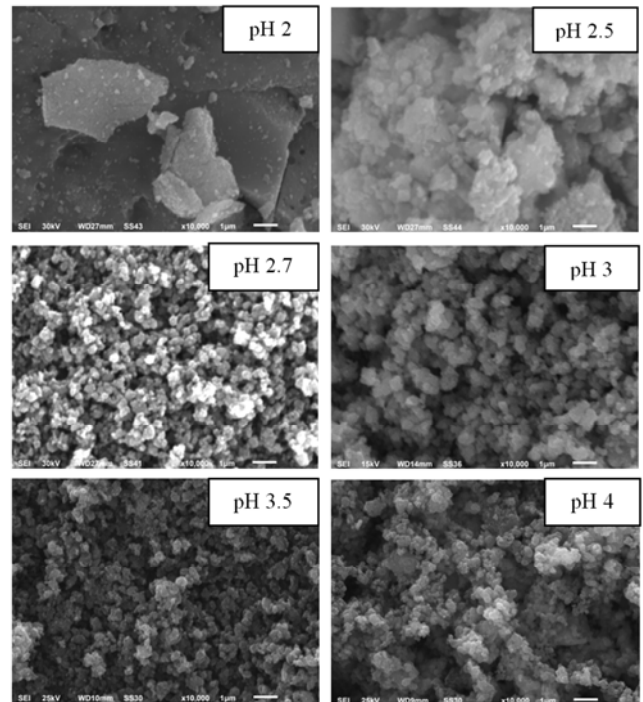


Figure 3. SEM images of TiO_2 prepared at different pH values.

Figure 3 shows the morphology of TiO_2 nanoparticles prepared at different pH value. All samples were annealed at 500°C . It is clear from figure 3 that the particle size of TiO_2 is decreasing by the increasing in pH value where all images were taken at magnification equal $1\ \mu\text{m}$. these results have a good agreement with XRD results.

From XRD analysis and SEM images of these samples, the sample which was prepared at 3 level of pH value is the most mixed phase sample according to calculations that were shown in table 1. Mixed phase TiO_2 nanoparticles are preferred for photocatalyst and optoelectronic applications.

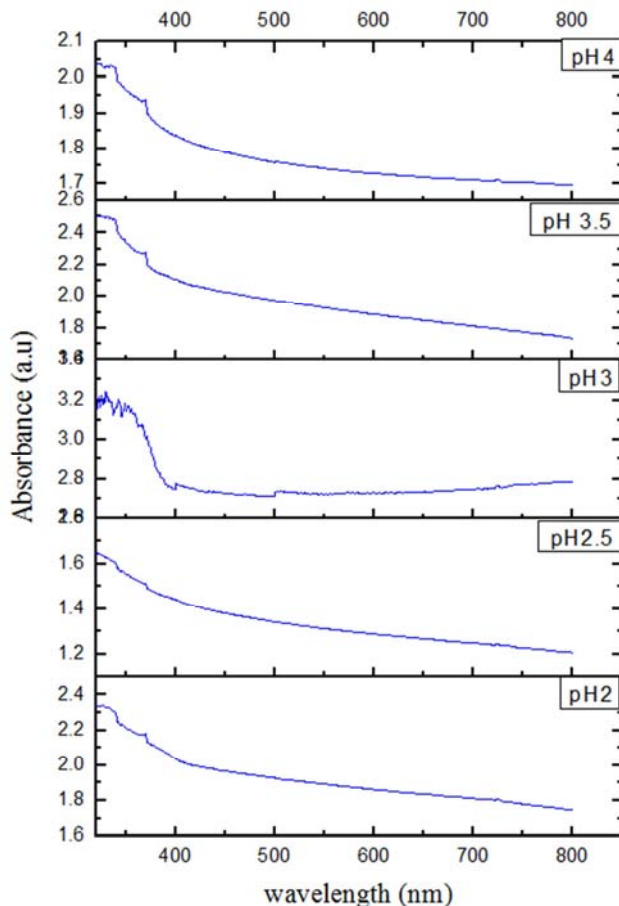


Figure 4. UV-vis spectrum of TiO₂ nanoparticles at different pH values.

Figure 4 shows UV-vis spectrum of different samples. It is clear that optical edge of TiO₂ about 380 nm and calculated band gap was found to be 3.14 eV as shown in figure 5.

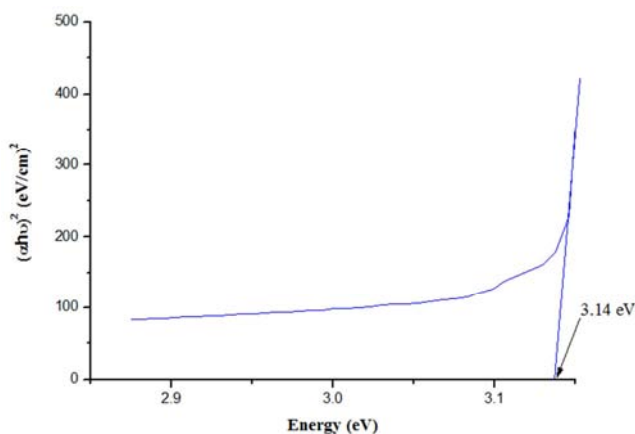


Figure 5. Band gap calculation curve of TiO₂ nanoparticles prepared at 3 levels of pH value and annealed at 500°C.

4. Conclusion

In this work, the pure and mixed phases of TiO₂ nanoparticles have been successfully grown by Sol-gel processing. XRD analyses of our samples show that AR transformation taken place at pH value lower than 3.5 levels.

SEM images of all samples show that grain size of TiO₂ decrease with increasing of pH value. This has a good agreement with XRD results. The calculated band gap of TiO₂ in this work is found to be about 3.14 eV.

References

- [1] Yin, H. et al. *Synthesis of ultrafine titanium dioxide nanowires using hydrothermal method*. Materials Research Bulletin, 2012. 47(11): p. 3124-3128.
- [2] Fujishima, A. *Electrochemical photolysis of water at a semiconductor electrode*. nature, 1972. 238: p. 37-38.
- [3] Li, Y.-F. et al. *Mechanism and activity of photocatalytic oxygen evolution on titania anatase in aqueous surroundings*. Journal of the American Chemical Society, 2010. 132(37): p. 13008-13015.
- [4] Chen, X. et al. *Semiconductor-based photocatalytic hydrogen generation*. Chemical reviews, 2010. 110(11): p. 6503-6570.
- [5] O'regan, B. and M. Grätzel, *A low-cost, high-efficiency solar cell based on dye-sensitized*. nature, 1991. 353(6346): p. 737-740.
- [6] Macwan, D. P. N. Dave, and S. Chaturvedi, *A review on nano-TiO₂ sol-gel type syntheses and its applications*. Journal of Materials Science, 2011. 46(11): p. 3669-3686.
- [7] Tada-Oikawa, S. et al. *Titanium Dioxide Particle Type and Concentration Influence the Inflammatory Response in Caco-2 Cells*. International journal of molecular sciences, 2016. 17(4): p. 576.
- [8] Mo, S.-D. and W. Ching, *Electronic and optical properties of three phases of titanium dioxide: rutile, anatase, and brookite*. Physical Review B, 1995. 51(19): p. 13023.
- [9] Cromer, D. T. and K. Herrington, *The structures of anatase and rutile*. Journal of the American Chemical Society, 1955. 77(18): p. 4708-4709.
- [10] Baur, W. *Über die Verfeinerung der Kristallstrukturbestimmung einiger Vertreter des Rutiltyps. III. Zur Gittertheorie des Rutiltyps*. Acta Crystallographica, 1961. 14(3): p. 209-213.
- [11] Kandiel, T. A. et al. *Tailored titanium dioxide nanomaterials: anatase nanoparticles and brookite nanorods as highly active photocatalysts*. Chemistry of materials, 2010. 22(6): p. 2050-2060.
- [12] Clark, R. J. H. *chemistry of titanium and vanadium; an introduction to the chemistry of the early transition elements*. 1968.
- [13] Aoki, Y. et al. *Insulating titanium oxynitride for visible light photocatalysis*. arXiv preprint arXiv:1701.06251, 2017.
- [14] Linsebigler, A. L. G. Lu, and J. T. Yates Jr, *Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results*. Chemical reviews, 1995. 95(3): p. 735-758.
- [15] Spanos, N. et al. *Electro-kinetic measurements on plugs of doped titania*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1998. 141(1): p. 101-109.

- [16] Banfield, J. *Thermodynamic analysis of phase stability of nanocrystalline titania*. Journal of Materials Chemistry, 1998. 8(9): p. 2073-2076.
- [17] Zhang, H. and J. F. Banfield, *Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: insights from TiO₂*. The Journal of Physical Chemistry B, 2000. 104(15): p. 3481-3487.
- [18] Ranade, M. et al. *eld, SH Elder, A. Zaban, PH Borse, SK Kulkarni, GS Doran and HJ Whitfield*. Proc. Natl. Acad. Sci. US A, 2002. 99: p. 6476.
- [19] Arbiol, J. et al. *Effects of Nb doping on the TiO₂ anatase-to-rutile phase transition*. Journal of Applied Physics, 2002. 92(2): p. 853-861.
- [20] Vogel, R. P. Hoyer, and H. Weller, *Quantum-sized PbS, CdS, Ag₂S, Sb & Bi particles as sensitizers for various nanoporous wide-bandgap semiconductors*. J. Phys. chem, 1994. 98(12): p. 3183-3185.
- [21] Gribb, A. A. and J. F. Banfield, *Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO₂*. American Mineralogist, 1997. 82(7-8): p. 717-728.
- [22] Ding, X.-z. and X.-h. Liu, *Correlation between anatase-to-rutile transformation and grain growth in nanocrystalline titania powders*. Journal of materials research, 1998. 13(09): p. 2556-2559.
- [23] Akarsu, M. et al. *A novel approach to the hydrothermal synthesis of anatase titania nanoparticles and the photocatalytic degradation of Rhodamine B*. Turkish Journal of Chemistry, 2006. 30(3): p. 333-343.
- [24] Qiu, S. and S. J. Kalita, *Synthesis, processing and characterization of nanocrystalline titanium dioxide*. Materials Science and Engineering: A, 2006. 435: p. 327-332.
- [25] Rath, C. et al. *Oxygen vacancy induced structural phase transformation in TiO₂ nanoparticles*. Journal of Physics D: Applied Physics, 2009. 42(20): p. 205101.
- [26] Orendorz, A. et al. *Phase transformation and particle growth in nanocrystalline anatase TiO₂ films analyzed by X-ray diffraction and Raman spectroscopy*. Surface Science, 2007. 601(18): p. 4390-4394.
- [27] Okada, K. et al. *Effect of Silica Additive on the Anatase-to-Rutile Phase Transition*. Journal of the American Ceramic Society, 2001. 84(7): p. 1591-1596.
- [28] Shin, H. et al. *Crystal phase evolution of TiO₂ nanoparticles with reaction time in acidic solutions studied via freeze-drying method*. Journal of Solid State Chemistry, 2005. 178(1): p. 15-21.
- [29] Matthews, A. *The crystallization of anatase and rutile from amorphous titanium dioxide under hydrothermal conditions*. American Mineralogist, 1976. 61(5-6): p. 419-424.
- [30] Spurr, R. A. and H. Myers, *Quantitative analysis of anatase-rutile mixtures with an X-ray diffractometer*. Analytical Chemistry, 1957. 29(5): p. 760-762.
- [31] Liu, G. et al. *Titania-based photocatalysts—crystal growth, doping and heterostructuring*. Journal of Materials Chemistry, 2010. 20(5): p. 831-843.
- [32] Hurum, D. C. et al. *Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO₂ using EPR*. The Journal of Physical Chemistry B, 2003. 107(19): p. 4545-4549.
- [33] Bakardjieva, S. et al. *Transformation of brookite-type TiO₂ nanocrystals to rutile: correlation between microstructure and photoactivity*. Journal of Materials Chemistry, 2006. 16(18): p. 1709-1716.