Mehran University Research Journal of Engineering and Technology

https://doi.org/10.22581/muet1982.2203.16

2022, 41(3) 161-167

# Effect of temperature on the polymorphs of titania ($TiO_2$) developed by sol-gel and hydrothermal processes for thin film uses

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Received: 24 April 2021, Accepted: 30 November 2021, Published: 01 July 2022

K E Y W O R D S

Titanium dioxide

Anatase

Nano-film

Sol-gel

Hydrothermal

Low temperature

A B S T R A C T

Titanium dioxide ($TiO_2$) has been utilized for photovoltaic devices mostly as electron selective ply. Most of the transition metal complexes like $TiO_2$ possess wider band gap to predominant relying on morphology of nano-particles. Most of the metal oxides possess excellent ability of harvesting extensive part of sunlight. This study reports, synthesis of $TiO_2$ by using two different techniques i.e., sol-gel and hydrothermal. Later nano films was applied on fluorine doped tin oxide glass through spin coating at ambient temperature. Particles of $TiO_2$ were synthesized at different temperatures however rest of the variable like solvent, concentration and amount of precursor were static. Nanoparticles of anatase titania synthesized through sol-gel had higher crystallinity. Particle size of synthesized particles was 12.2 nm at 25° C. Subsequently particles produced through hydrothermal procedure were large with an average particle size of 16 nm at 100° C. FTIR further confirmed the synthesis of anatase titania at 400-800 $cm^{-1}$. X-ray diffraction technique also confirmed the synthesis of titania at 25.3°, 38.0°, 47°, 54.5°, 62.7° and 78°. UV-visible spectroscopy was performed to analyze optical properties exhibiting peak absorbance at 424 nm. This synthesized $TiO_2$ anatase is extensively used for photovoltaic application.

## 1. Introduction

Metal oxide nanoparticles are regarded as valuable material and are often synthesized and learnt intensively. Metal oxide nanoparticles show different physiochemical behaviors compared to bulk compounds with the improved optical, surface, thermal and electrical properties [1-2]. $TiO_2$ is the most prevalent titanium compound that has always been under constant investigation and development over the past several decades amongst the numerous transition metal oxides and found essential applications in a wide variety of fields [3-4]. Titania is non-toxic biocompatible, inexpensive material that exhibits excellent photo efficiency and photoactivity. Titania is widely used for drug delivery [5-6], biosensing [7], water purification [8], catalysis [9], photocatalysis [10], dye-sensitized solar cell [11], sensors [12], chromatographic packing [13], pigments [14], wastewater treatment [15], self-cleaning [16], environmental analytical chemistry [17] and biomedical applications [18]. Chemistry of titania is comparatively multifaceted as it may occur in crystalline and amorphous forms, containing rutile, anatase, brookite, or the combination of all three. Mostly it exists anatase and rutile phase with tetragonal structure. Brookite phase possess crystalline orthorhombic structure [19]. For the white pigment application rutile

is consumed due to its ability to protect against ultraviolet light and is only thermodynamically stable at all temperatures and pressure [20]. Anatase and brookite are metastable phases when heated they quickly turn into rutile [21]. Anatase phase of titania is generally favorable during most of the synthesis processes due to its formation at low temperature. Previously, $TiO_2$ nanomaterials synthesized by conventional methods for example sol-gel [22], hydrothermal [23], flame synthesis [24], solvothermal [25], dialysis- hydrolysis [26], alcohothermal method [27], molecular assembly [28], sputtering [29] and chemical vapour deposition [30]. Nanoparticle of titania are produced by conventional bottom up techniques that require special handling and are lengthy, subtle and costly. The parameters that significantly influence the formation of anatase include procedural reaction time, pressure and temperature. Besides these, secondary operation during synthesis also play crucial part in the formation of anatase [31-32]. Whereas chemical composition, morphology and composition of phase can be optimized by pH, and temperature by employing hydrothermal and sol-gel techniques [33]. However, hydrothermal method works at a temperature above 200 $^oC$ which is very high and imparts influence on morphology of titania [34-35].

Properties of titania mostly depends on its crystal phase and surface morphology. The known highly photoactive form of titania is anatase, that is widely used for photovoltaic operation for harvesting solar energy with an energy band gap of approximately 3.2 eV [36].

Recent study suggests that, processing and chemical substances used during synthesis of titania are responsible for chemical and physical attributes of the solar [37]. However, crystal structure, surface area, chemistry of surface and photo behavior are also responsible feature for potential photo efficiency. The specific structure of the energy band leads to the increased photoactivity [38]. Anatase phase is usually achieved below the temperature of 600 $^oC$ and can be transformed into Rutile phase above 800 $^oC$. Efficiency of photoactive materials depends on the phase, crystal structure and morphology and these factors rely on synthesis methods [39]. Hence it is need of time to optimize the prescribed conditions for developing efficient titania for thin film applications.

Herein, hydrolysis of titanium alkoxide was carried out in presence of an acid catalyst, that assisted hydrolysis [40]. Since, chemical stability of titania relies on the synthesis temperature. Titania is synthesized under different temperatures through hydrothermal and sol-gel methods in presence of acetic acid and temperature was optimized for thin film applications.

## 2. Materials and Methods

### *2.1 Materials*

Titanium tetraisopropoxide (TTIP, 98%) was purchased from DEAJUNG, Republic of Korea was used as precursor for the synthesis of $TiO_2$. Ethanol ($C_2H_6O$, 99.8%) was brought from Merck KGaA and acetic acid (99.5%) were procured from Panreac, Barcelona, Spain.

### *2.2 Synthesis of $TiO_2$ by Sol-Gel Method*

Synthesis of $TiO_2$ was done by employing sol-gel method as reported by Wang et al [41]. A mixture of TTIP (4 mL) with ethanol (40 mL) with subsequent stirring using hot plate magnetic stirrer at the different temperature for 30 min. Later beaker was placed in sonicator for 30 min. Afterward, 9 mL of acetic acid was added, and left for 3 h with continuous. Subsequently, the pH of the suspension was changed with 20 mL of ethanol 1M NaOH solution. Finally, the particles were rinsed using deionized water, and dried for 12 h at 100 $^oC$ and heat treated at 350 $^oC$ in muffle furnace for 2 h.

### *2.3 Synthesis of $TiO_2$ by Hydrothermal Method*

Hydrothermal synthesis of titania was done by adding titanium tetrapropoxide in ethanol. Later prepared mixture of TTIP (4 mL) and ethanol (40 mL) was stirred using a hot plate magnetic stirrer for 30 min. After this the beaker was placed in a sonication for 30 min. Afterward, 9 mL of acetic acid was added, and the stirring was left for 3 h. After this, the pH of the suspension was changed with 20 mL of ethanol 1M NaOH solution. The reaction is then shifted in an autoclave of 100 mL and further heated for 12 h at different temperatures and left to cool at ambient temperature. Eventually, the particles were cleaned with deionized water, and left for drying for 12 h at 100 $^oC$ subsequently after the moisture was expelled the synthesized particles were heat treated at 350 $^oC$ in muffle furnace for 2 h.

Specimens were labelled as HT-X for the hydrothermal process and SG-X for the sol-gel process, respectively. The X denotes to different temperature for synthesis.

### *2.4 Characterization*

Phase composition and crystalline size of synthesized $TiO_2$ was evaluated by using XRD Diffractometer. XRD patterns were recorded using BRUKER D8 ADVANCE (40 kV/30 mA) provided with Cu K radiation at a

scanning rate of 2 θ /min, in the 2θ range 20–80º. The crystalline size of the crystal was determined using Scherrer equation. To study the surface morphology of titania JEOL JSM-6380LV scanning electron microscope was used. FTIR spectroscopy was employed for the identification of synthesized $TiO_2$ and surface adsorption of functional groups on $TiO_2$ nanoparticles in transmission mode from 400 to 4000 $cm^{-1}$. UV-vis spectroscopy was done on Perkin Elmer Lambda 365, with a closed quartz cell to study the optical absorptions (optical path length: 1 cm). Relation between Photocurrent–voltage (I–V) was measured by using computerized digital multi-meters.

## 3. Result and discussion

### *3.1 Surface Analysis*

Surface topography of $TiO_2$ obtained through a two-step reaction using two different methods is shown in Figs. 1(a) and 1(b). Surface of synthesized $TiO_2$ exhibited complete dense and homogeneous. Micrograph also illustrate homogeneous sphere-like nanoparticles of anatase phase of $TiO_2$. Synthesized nanoparticles are homogeneous, with good interconnection between particles. Apart from a limited portion of aggregated nanoparticles, most of nanoparticles of $TiO_2$ retained their original spherical geometry, confirming strong stability of the synthesized nanoparticles. Synthesized particles were in arranged and agglomerated in a regular pattern. It is possible that amorphous surface of crystalline structure may cause nanoparticles to join or connect with the particles of high surface area. Furthermore, the larger particle size in the porous structure may be due to the physical aggregation of tiny nanoparticles [42].

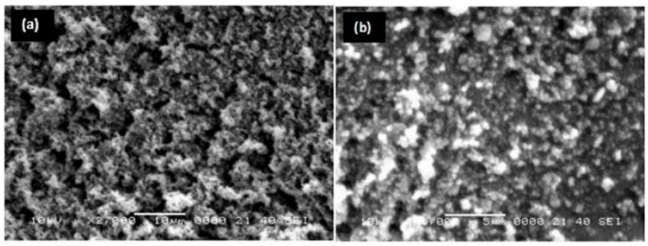


**Fig. 1.** SEM images of (a) Titania prepared by hydrothermal and (b) sol-gel methods

### *3.2 Phase Analysis*

Diffraction patterns of $TiO_2$-SG and $TiO_2$-HT as shown in Figs. 2(a) and 2(b) were studied using High Score plus exhibit diffraction peaks at 2θ values of 25º, 38º, 47º, 54º, 62º, and 78º respectively, that corresponds to diffracted planes (101), (112), (200), (105), (204), and (206), which is attributed to the anatase tetragonal crystal structure of $TiO_2$. Specimens were synthesized using hydrothermal and sol-gel procedures. It is pertinent to note here that peaks of rutile, and brookite did not exist, which further validates the phase purity of the synthesized specimens. Diffracted peaks illustrated in Figs. 2(a) and 2(b) are indexed to JCPDS card no. 00-021-1272 that are referenced for Titania synthesis by hydrothermal and sol-gel methods respectively. Crystalline size of $TiO_2$-SG and $TiO_2$-HT was evaluated using Scherrer equation and found average sizes of 13.6 nm and 21.7 nm, respectively. This incremental trend in crystal size for specimen synthesized via hydrothermal procedure is due to hydrothermal temperature. Crystalline size for specimens developed via hydrothermal method were found 16.02 nm, 16.6 nm and 32.52 nm at 80 °C, 100 °C and 120 °C respectively. It is concluded that increase in temperature during hydrothermal process provides adequate energy for crystal size [43].

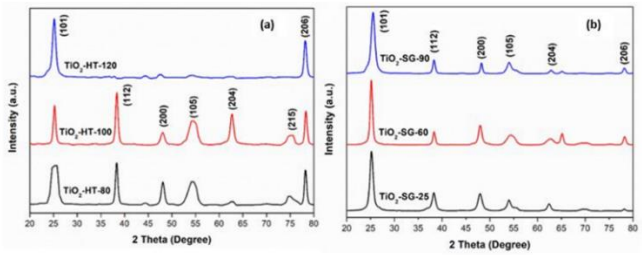


**Fig. 2.** XRD peaks of Titania (a) Hydrothermal, (b) Sol-gel

### *3.3 Functional Group Analysis*

FTIR spectroscopy was carried out for the specimen prepared by sol-gel and hydrothermal techniques. Figs. 3(a) and 3(b), exhibit finger prints of titania with anatase phase bends at 3426 $cm^{-1}$ and 3437 $cm^{-1}$ are attributed to faces of physisorption of O-H bond present in water, stretching on $TiO_2$ spectra at 1400 $cm^{-1}$ – 1640 $cm^{-1}$ represents the bending of O-H modes. Spectrum at 1400 $cm^{-1}$ and 1430 $cm^{-1}$ is due to the vibration of carbon in precursor group of sol-gel. Bands between 500-1000 $cm^{-1}$ represents the skeletal frequency zone of Ti-O-Ti and Ti-O, C=O, O-C=O functional groups are only identified in samples synthesized with sol-gel process. However, specimen synthesized by hydrothermal have no such evidence, this could be due to high pressure and temperature in hydrothermal process. However, appearance of spectra maybe due to the reaction between acetic acid, TTIP and ethanol. Previous studies has also report the existence of these groups [44, 45]. These are designated to the Ti-O interface bond with organic compounds present in reaction medium. FTIR further concludes that all the synthesized samples exhibit

identical bend for both methods, and no significant variation is formed between samples.

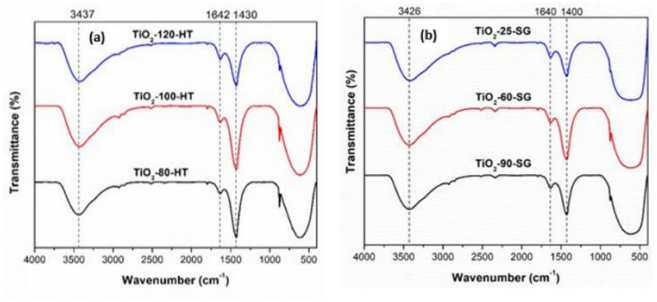


**Fig. 3.** FTIR spectra of (a) hydrothermal and (b) sol-gel samples

*3.4 Optical Analysis*

Analysis of UV absorption for $TiO_2$-HT and $TiO_2$-SG are shown in Figs. 4(a) and 4(b). Spectrum exhibits the effect of titania synthesized by hydrothermal and sol-gel techniques in UV and visible light spectrum. Spectrum shows prominent surge in absorption at 425 nm due to electron excitation from visible to conduction band of $TiO_2$ semiconductor [46, 47].

$E_g$ is explained by plotting $(\alpha hv)^2$ vs. $hv$ (direct transitions) where $v$ is the frequency, $h$ is the Planck constant and $\alpha$ is the absorption coefficient. The absorption coefficient of titania nanoparticles was calculated using equation, $(\alpha hv)^2 = hv = E_g$.

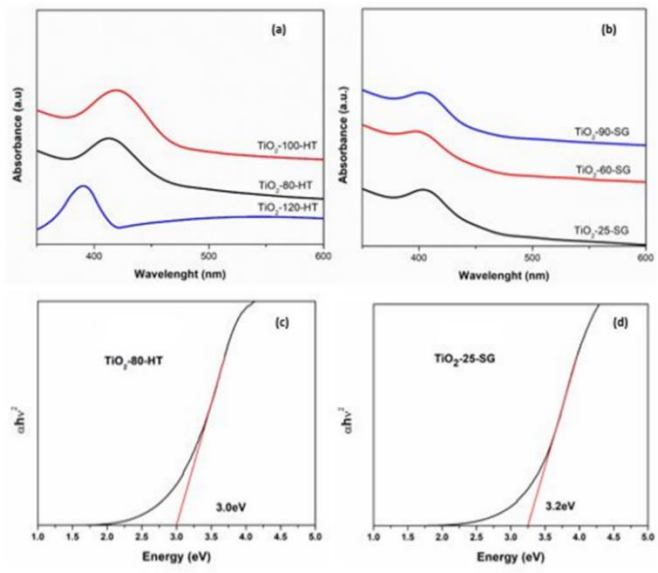


**Fig. 4.** UV-visible spectrum of $TiO_2$ (a) bandgap energy of Hydrothermal and (b) sol-gel samples

In Figs. 4(c) and (d), Eg values obtained from the titania produced from in sol-gel and hydrothermal were 3.2 and 3.0 eV respectively. The slight blue-shift in the absorption band edge in $TiO_2$ has been attributed to excitation confinement as particle size decreases (known as quantum size effect). The blue-shift of the optical energy gap has caused a shift in energy gap of the disordered crystal in $TiO_2$ nano powders. The particle size of $TiO_2$ (anatase) produced through hydrothermal process enhanced from 13.6 to 21.7 nm due to increased thermal effect, whereas the corresponding optical energy difference estimated to be 0.25 eV. The bandgap energy decreased due to the expansion of crystal lattice and breakage of interatomic bonds break due to hike in temperature. Due to the scientific fact that weaker bonds require less energy to split and allow an electron to enter the conduction band [48].

*3.5 Electrical Analysis*

Figs. 5(a) and 5(b) shows the electrical attributes of $TiO_2$ prepared by hydrothermal and sol-gel techniques. The applied bias voltage was measured with the semiconductor analyzer and probe-station. The $TiO_2$ mounted on the FTO glass substrate has IV properties ranging from 0V to 25V. When a forward bias voltage is applied, Titania displays the conductive state, in sol-gel method due to its good bandgap than hydrothermal as shown by the linear I-V curve scale. Despite the fact that a linear relationship of characteristics implies that the nature of the interface is linear and ohmic in $TiO_2$-25-SG [49-51].

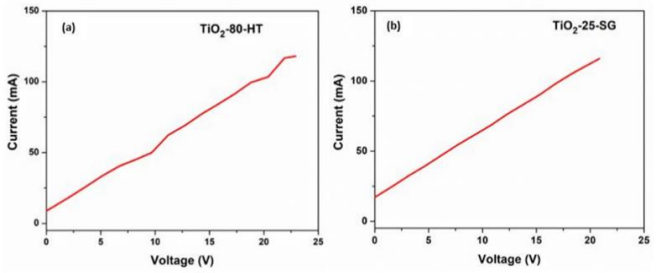


**Fig. 5.** I-V curve of (a) hydrothermal and (b) sol-gel samples

## 4. Conclusion

This study concludes that nanoparticles of $TiO_2$ were synthesized at different temperatures (<200) through sol-gel and hydrothermal techniques. Applications of synthesized material as PV material was investigated and influence of temperature on photoactivity of titania was also studied. Morphological and structural analyses confirmed the pure anatase was attained in both synthesis methods. Also, for photovoltaic applications, the electrical and optical properties of Titania nanoparticles was done with increased efficiency. The technique is simple and environmentally friendly, and it can be scaled up to industrial levels. This finding supports the concept that anatase nanoparticles derived by sol–gel and hydrothermal methods could be used as potential materials for thin films in photovoltaic devices

and lithium-ion batteries, Furthermore, it is suggested that titania can used for developing nanocomposites for various photovoltaic applications.

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