

Investigation on the Phase Transition and Morphology of TiO₂ Nanoparticles with respect to Calcination Temperature

G. NAGARAJ, Dr. A. Dhayal Raj, Dr. A. Albert Irudayaraj

¹Research scholar, SHC-Tirupattur, ²Assistant Professor, SHC-Tirupattur

³Associate Professor, SHC-Tirupattur

Department of Physics

Sacred Heart College, Tirupattur, Vellore District, Tamilnadu, India-635601.

Abstract: Pure TiO₂ nanoparticles have been prepared by a novel Photon Induced Method (PIM) without precursor modification. The prepared sample has been calcinated at 500°C, 700°C and 1000°C to study the effect of calcinations temperature on the stability, phase and morphology of TiO₂. XRD analysis reveals an interesting result of increase in phase stability. This may be accounted to the oxygen richness of the sample which has been confirmed through EDAX. XRD results also reveal a phase transformation from anatase to rutile with increasing calcination temperature. The morphologic analysis performed with HRSEM and HRTEM reveal a transformation from nanoparticles to nanorods. The formation of TiO₂ is confirmed through the Ti-O vibrational peaks in FTIR and the band gap of the samples have been examined with UV-vis Spectrophotometer. The prepared samples with such high phase stability may be applied for photocatalytic application.

Key world: Pure TiO₂, PIM, Stability, HRTEM and UV-vis analysis

1. Introduction

Titania has been widely studied to address environmental and energy crises. The development of highly active heterogeneous photocatalysts has attracted a great deal of attention in recent years [1-4]. Titanium dioxide has been receiving considerable attention because of its strong oxidizing power, appropriate valence band and conduction band positions, non-toxicity and long-term stability. In natural history, Titania has polymorphs namely, anatase, rutile and brookite. Anatase is a metastable phase while the rutile is a stable phase. Generally, anatase displays much higher photocatalytic activities than rutile phase [5-7]. However, the detailed morphologies and particle size affecting the photocatalytic activity among anatase and rutile is still under argue. Generally, the photocatalytic activity of Titania is strappingly dependent on its specific surface areas, phase, structure, morphologies and crystallite size [8-10]. The anatase may be accounted to its higher photocatalytic activity because of higher surface adsorption capacity to hydroxyl groups and a lower charge carrier recombination rate than rutile. The lower photocatalytic activity of rutile is also related to its larger grain size, lower specific surface areas and having a poorer surface adsorption capacity [11-14].

In addition, the morphologies and crystalline size have a significant influence on the transfer, separation and mobility of photogenerated electron and hole pairs. However, the full potential application of anatase TiO₂ is hampered by its activation only to UV irradiation. Therefore, current research has sought to improve the properties of Titania by extending the absorption of titania to visible light region [15-22]. Precursor modification using H₂O₂ has been demonstrated to be one of the effective routes to achieve the same. In the present work, we propose a facial Photon Induced Method (PIM) for the preparation of oxygen-rich pure anatase titania nanoparticles. Moreover, explanation regarding the tailoring of the properties of the prepared anatase titania, so as to utilize visible light has also been presented here.

2. Catalyst preparation

Oxygen-rich Titania were grown by photon induced method by mixing required amount of Ti(OPr)₄ with 1000 ml of Double Distilled water and the solution is stirred for 7 hrs under the irradiation of 250 W halogen light. The solution was then left undisturbed in the dark for 17 hrs. The same procedure is followed for 2 days. 400 ml of water is added everyday day. The solution is kept in open place day and night for 6 days. Finally ammonia is added and the solution was exposed to halogen light without adding water. The final powder thus obtained is collected and calcinated for 1 hr at 500°C, 700°C and 1000°C.

3. Results and Discussion

3.1 Powder XRD analysis

The XRD patterns of the TiO₂ samples calcinated at 500°C and 700°C shown in fig. 1(a and b) are typically of anatase phase TiO₂ matching with the JCPDS No# 21-1272. No diffraction peaks due to the rutile phase are observed. This indicates that the synthesized samples are truly of pure anatase phase. The XRD pattern of the sample calcinated at 1000°C in fig. 1c corresponds to typical rutile phase TiO₂ matching with JCPDS No# 21-1276. No diffraction peaks due to the anatase phase are observed. This indicates that the synthesized samples are truly in pure rutile phase when calcinated at 1000°C. It is surmised that the sample calcinated at 1000°C with rutile phase is highly crystalline; this is confirmed by the low value of its Full Width Half Maximum (FWHM). This is also indicative of a large crystallite size of 110 nm for sample calcinated at 1000°C while the crystallite size of 10 nm and 15 nm is obtained for samples calcinated at 500°C and 700°C respectively.

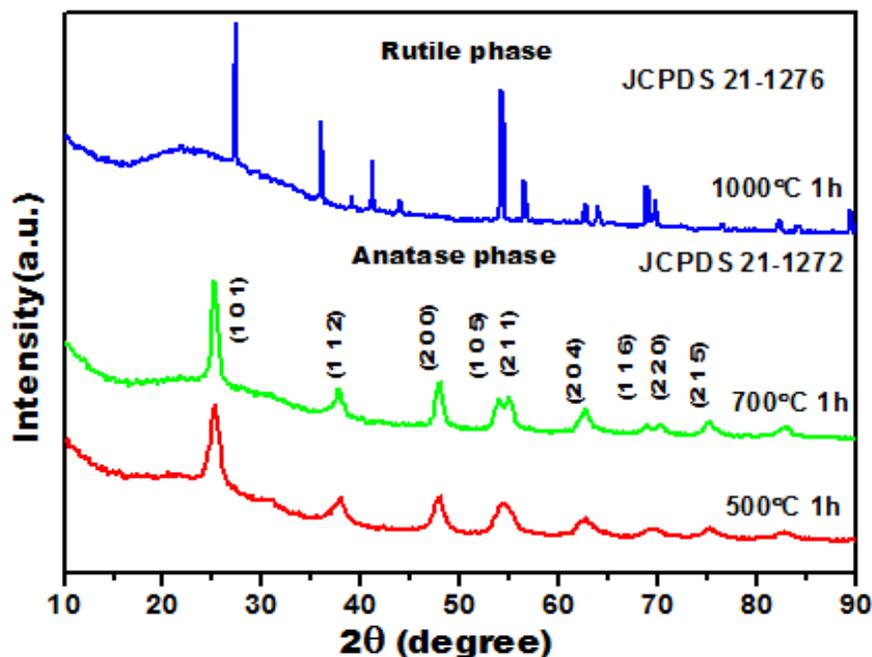


Fig.1 The power XRD patterns of TiO_2 sample calcinated at (a) 500°C, (b) 700°C and (c)1000°C

3.2 HRSEM and HRTEM Micrograph analysis

Fig. 2 (a and b) shows the HRSEM micrographs to study the surface morphology of anatase and rutile samples. However no clear information could be gathered except the appearance of clumsy particles. The HRTEM image obviously shows the morphology as spherical nanoparticles of size 32 nm and 45 nm as seen in fig. 3(a and b), corresponding to samples calcinated at 500°C and 700°C respectively. While the micrograph in fig.3c corresponding to the TiO_2 sample calcinated at 1000°C, shows nanoparticls and nanorod like morphologies. The measurement of the isolated nanorod is 210 nm wide and 350 nm length (fig.3c). This results confirm the increase in particle size as the calcination temperature is increased. Moreover a transformation of morphology from nanoparticles to nanorod is witnessed along with the phase transformation from anatase to rutile.

Fig.2 HRSEM images of TiO_2 sample calcinated at (a) 500°C, (b)700°C and (c)1000°C

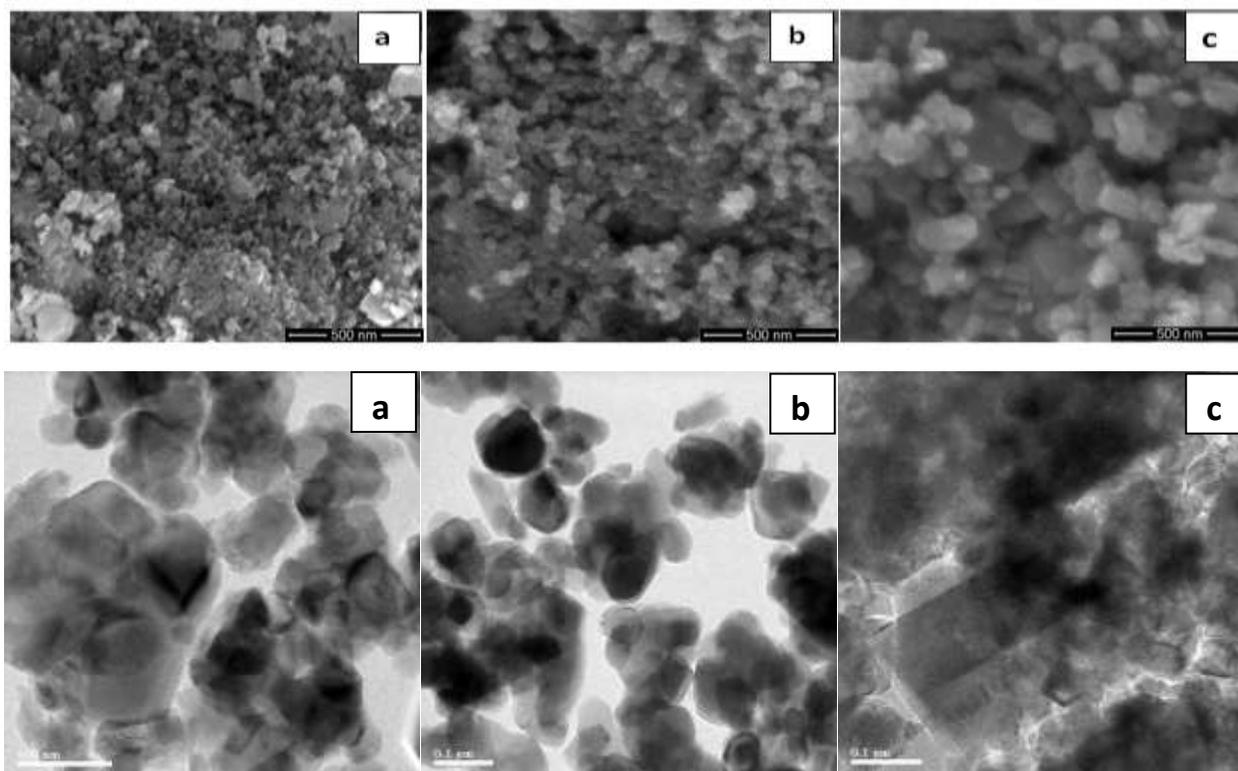


Fig.3 HRTEM images of TiO_2 sample calcinated at (a) 500°C, (b) 700°C and (c)1000°C

3.3 FTIR analysis

Fig. 4 shows the FTIR spectra of samples calcinated at 500°C, 700°C and 1000°C with anatase and rutile phases. The peak around 1043 cm^{-1} may be due to C-O stretching [23]. The peak around 1656 cm^{-1} correspond to the hydroxyl groups of molecular water [24] and a broad peak at 3430 cm^{-1} for the O-H stretching vibrations. The small peaks at 2854 and 2921 cm^{-1} in the spectrum may be attributed to the CH_2 stretching vibrations [25]. Fig.4 (a and b) shows the FTIR measurement for the anatase phase TiO_2 calcinated at 500°C and 700°C samples. It can be observed that the intensities of absorption bands of oxygen-containing functional groups such as C-O (1043 cm^{-1}) are gradually reduced with increase in calcinations temperature. This results indicate that as the calcination temperature is increased, the oxygen content in the sample is reduced. The spectrum also showed strong absorption bands at 720 cm^{-1} indicating the presence of Ti-O-Ti bond in TiO_2 as shown in fig 4(a, b and c) [26].

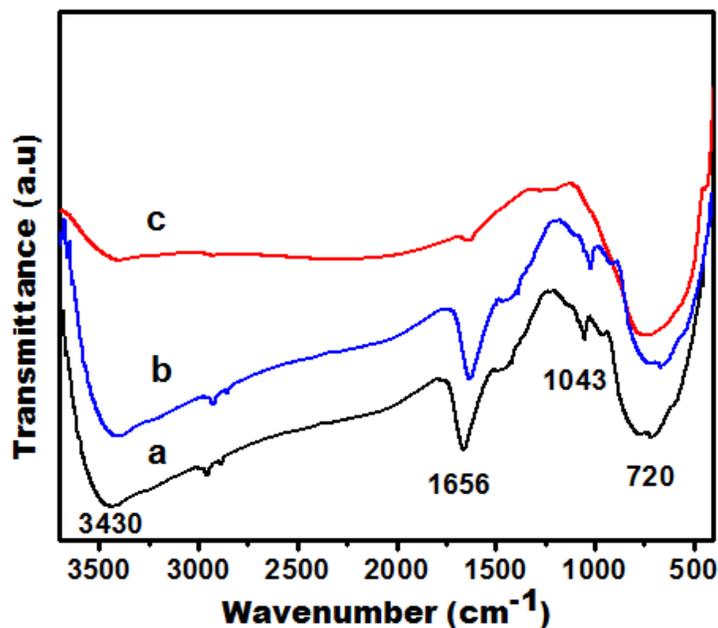


Fig.4 FTIR spectrum of TiO_2 sample calcinated at (a) 500°C, (b)700°C and (c)1000°C

3.4 UV-vis analysis

UV-visible (UV-vis) spectroscopy has been proven to be an effective optical characterization technique to understand the bandgap of semiconductors. The optical band gap of TiO_2 are determined using a Tauc plot as shown in Fig. 5(a, b and c). The approximate band gap of pure TiO_2 sample calcinated at 500°C, 700°C and 1000°C are 3.2 eV, 3.08 eV and 2.97 eV respectively. This supported the qualitative observation of a red shift in the absorption edge of the pure anatase phase TiO_2 calcinated at 700°C compared to the sample calcinated at 500°C. The narrowing of band gap could be ascribed to the chemical bonding (oxygen-rich) between TiO_2 and the specific sites of carbon during the Photon induced method.

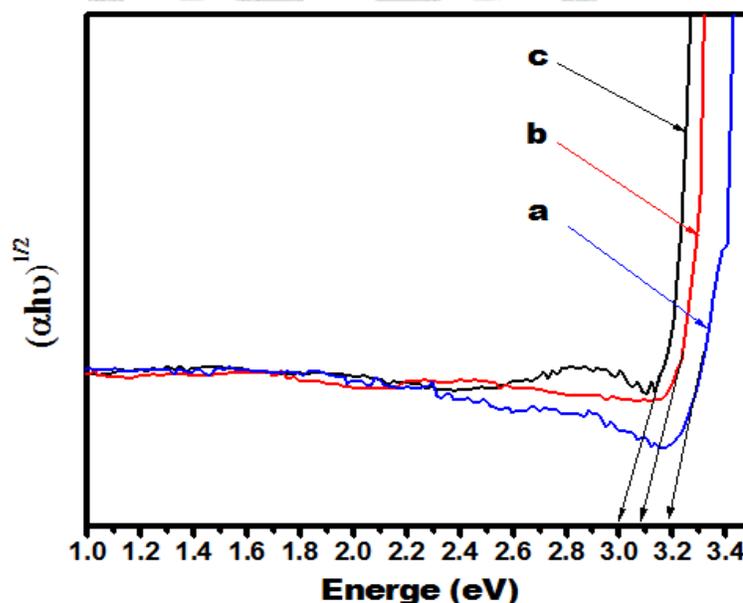


Fig.5 UV-visible spectroscopy of TiO_2 calcinated at (a) 500°C, (b)700°C and (c)1000°C

4. Conclusion

The photon induced method is used to prepare oxygen rich TiO₂. The structures, morphology and band gap of the sample has been analyzed with respect to increase in calcinations temperature. XRD result show that, as the calcinations temperature increases an anatase to rutile phase change is witnessed. Moreover, the increase in peak intensities suggests a decrease in full width at half maximum which in turn exposes an increase in crystallite size. The HRTEM images show a morphology transformation from nanoparticles to nanorods with increasing calcinations temperature. This suggests that calcinations temperature also plays a vital role in directing the morphology and crystalline nature. The optical bandgap calculated shows a decreasing trend with increase in calcination temperature. Thus the band gap of the oxygen-rich TiO₂ prepared by PIM is engineered so as to absorb energy in the visible light region. This will open new insight into various applications such as photocatalytic activity, solar cells, antibacterial activity, killing of cancer cells and so on.

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