Development of pure rutile TiO_2 and Magneli titanium sub-oxide microstructures over titanium oxide-seeded glass substrates using surfactant-free hydrothermal process

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Abstract. Titanium oxide seed layer was coated over glass substrates by sol-gel spin coating method. Single-step surfactant-free hydrothermal process developed titanium oxide microstructures over the titanium oxide-seeded glass substrates. Various morphologies of titanium oxide microstructures, varying from coral reefs to flower-like morphology were evolved by changing HCl concentration (1 and 3 M) in the precursor solution and growth temperature (GT) (120, 150 and 180°C) of the hydrothermal process. Structural studies confirmed the formation of rutile TiO_2 , $\text{TiO}_2 + \text{Ti}_2\text{O}_3$ and Ti_4O_7 microstructures due to varying the concentration of HCl (1 and 3 M) in the solution and GTs. Morphological studies revealed the possibility of engineering coral reefs, cauliflower, flowers, ball, cactus and jasmine flower-shaped microstructures of titanium oxide films by tuning the growth parameters. The indirect band gap of the titanium oxide microstructures derived from UV-Vis absorption spectra lies in the range of 2.9–3.02 eV.

Keywords. TiO_2 ; titanium sub-oxides; film; hydrothermal method; microstructures.

1. Introduction

Designing and developing titanium oxide (TiO_2) nanostructures and microstructures via controlled growth to achieve various shapes, sizes and morphologies have been the focus of intensive research in the recent times, because the versatile and exotic properties of the nanostructures make them to find applications in solar cells [1], photocatalysts [2], sensors [3], hydrogen production [4] and tissue engineering scaffolds [5]. Various studies have proved that the physical and chemical properties and device performance of TiO_2 nano/microstructures strongly depend on their crystal system, dimension and morphology. Therefore, engineering the morphology of TiO_2 structures has gained importance and hence, various research groups have been working on synthesizing and engineering the TiO_2 nano/micro structures of TiO_2 [1–6].

Generally, TiO_2 exists in three different crystalline phases of rutile, anatase and brookite. Among them, rutile phase is thermodynamically stable, while anatase and brookite are metastable [7,8]. Even though the TiO_2 anatase is commonly accepted as active phase for photochemical applications [9], it is lacking in some properties like high chemical stability, dielectric properties, ultraviolet ray absorption rate and mechanical strength when compared to the corresponding

values of the rutile phase. Some of the literature reports show that rutile TiO_2 is also more active in photochemical applications compared to the anatase phase [10–12]. The general formula of titanium sub-oxides is $\text{Ti}_n\text{O}_{2n-1}$ (n is an integer between 3 and 10); titanium sub-oxides possessing the above chemical formula with n value between 3 and 10 is generally known as Magneli phases [13,14]. The titanium–oxygen system plays an important role in the study of non-stoichiometry of a material and most of them are used in various applications, due to their excellent conductivity and remarkable visible light absorptivity [15]. Li *et al* [16] fabricated the Ti_4O_7 ceramics using carbothermal reduction method under argon atmosphere and also at vacuum; and constructed the high conductive electrodes. Ioroi *et al* [17] prepared corrosion-resistant Magneli phase sub-stoichiometry titanium oxide (Ti_4O_7) to support the Pt catalysts. Suzuki and Takemoto [18] used Magneli phase Ti_4O_7 as a counter electrode that showed higher short-circuit current density than that of Pt counter electrode in dye-sensitized solar cell. Zhong *et al* [19] prepared novel 3D $\text{Si}/(\text{TiO}_2 + \text{Ti}_2\text{O}_3)$ composite nanorod arrays and used them as the anode in lithium ion batteries.

Several studies discuss the role of morphology of different nanostructures for various applications; however, there exist challenges in designing, synthesizing as well as tuning the surface morphology of the titanium oxide hierarchical

nano/microstructures on the glass substrates due to lattice mismatch between them. Challenges of this nature can be overcome by forming suitable seed layers on the glass substrates and then growing various nanostructures of the materials on the seeded glass substrates by tuning the growth parameters [20]. Various techniques such as, dip coating [21], sol–gel spin coating [20], spray pyrolysis [20] and chemical bath deposition [22] have been employed to prepare titanium oxide seed layer on glass substrates. Among the various methods, sol–gel spin coating method is of low cost and facilitates to optimize the film thickness with ease. Further tuning of the surface morphology of titanium oxide films has been achieved through several methods, such as sputtering [23], hydrothermal [24], sol–gel [25] and electro deposition [26]. Among these methods, the hydrothermal method is simple, and has the potential to tune the morphology of the materials easily by varying solution concentrations and growth parameters.

The present work is aimed to investigate the effect of various concentrations of HCl in the precursor solution as well as the growth temperature (GT) on tuning the morphology and hence, the structural and optical properties of titanium oxide deposited on titanium oxide seed layer formed on glass substrate via a surfactant-free hydrothermal process. Further synthesis of Ti_4O_7 and rutile $\text{TiO}_2 + \text{Ti}_2\text{O}_3$ hierarchical microstructures are reported for the first time over the titanium oxide seeded glass substrates through the hydrothermal process at various GTs without using surfactant.

2. Experimental

Titanium oxide seed layer was deposited by sol–gel spin coating method on the clean microslide glass substrates of $1.5 \times 1 \times 0.1$ cm dimensions. The required amount of titanium tetra isopropoxide (TTIP), ethanol and acetic acid were mixed together in a 50 ml beaker and stirred well for about 2 h at room temperature, which gives the final sol–gel solution. The prepared solution was dropped on the clean glass substrates. The acceleration speed of spin coater maintained at 3000 rpm for 30 s to deposit thin layer of titanium oxide, which was subsequently annealed at 450°C in a muffle furnace for about 4 h. Thickness of the deposited titanium oxide layer was about ~ 100 nm, which was used as seed layer for growing TiO_2 microstructures on it. Thus, the seed layer formed on the glass substrate avoids the peeling of the titanium oxide microstructured film by the hydrothermal process.

Double-distilled water (20 ml) and the required amount of HCl (1 and 3 M) were mixed under magnetic stirring for 15 min. Then, TTIP solution (0.2 ml) was added dropwise to this solution and stirred for about 30 min. The final clear growth solution obtained was transferred to a Teflon-lined stainless-steel autoclave and the substrate coated with titanium oxide seed layer was placed in the solution such that it was inclined at about 45° angle to the wall of Teflon with seed layer facing upward. Titanium oxide microstructures were

prepared employing the surfactant-free hydrothermal process by adding different volumes of HCl (1 and 3 M) in the precursor solution, in separate experiments at three different GTs of 120, 150 and 180°C for a growth period of 16 h each. Then, the autoclave was naturally cooled down to the room temperature. The seeded glass substrate containing the hydrothermally grown film was removed from the solution and dried at room temperature. The titanium oxide microstructures formed on the seed layer from HCl (1 M) added precursor solution at GTs 120, 150 and 180°C are named as 2A, 2B and 2C, respectively, and that of the microstructure film formed on the seed layer from the solution containing HCl (3 M) at GTs 120, 150 and 180°C are named as 5A, 5B and 5C, respectively. Structural properties of the films were studied from X-ray diffraction (XRD) analysis using PANalytical's X'pert pro with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The surface morphology of the synthesized films was analysed using JEOL-JSM 6390 scanning electron microscope (SEM). The optical absorption spectrum of the films was recorded using Shimadzu-UV 1800 double-beam spectrometer. The photoluminescence (PL) spectra were recorded by Floro Log-Horiba equipment using Xenon ionlaser.

3. Results and discussion

3.1 Structural properties

XRD pattern of the synthesized 2A, 2B, 2C, 5A, 5B and 5C films were recorded in the 2θ range of 10 – 80° . The XRD pattern of the 2A, 2B and 2C film (figure 1a) are compared with the standard JCPDS card no: 88-1175 (space group: $P4_2/mnm$), which confirms the formation of polycrystalline rutile tetragonal TiO_2 structure. No peaks of anatase or brookite phases are detected. The observed preferential growth in 2A, 2B and 2C films is along (110) plane. It is evident from figure 1a that when the GT increases, the intensity of the peak is also increased and hence, the crystallinity of synthesized TiO_2 films is improved. Figure 1b presents the XRD patterns of films 5A, 5B and 5C. The XRD peaks of film 5A compare well with JCPDS card data: 72-1724, which confirms the formation of Ti_4O_7 Magneli phase of titanium oxide. The XRD diffraction peaks of the film 5A (3 M HCl; GT 120°C) reveals the presence of Ti_4O_7 phase only with an intense XRD peak of (10 $\bar{2}$). The preparation of various Magneli phases of titanium oxides was reported employing various techniques, especially, Ioroi *et al* [26] and Zhu *et al* [27] prepared the Ti_4O_7 Magneli phase using carbothermal reduction treatment. The XRD peaks of film 5A microstructures confirm the formation of pure Ti_4O_7 Magneli phase, a first report from the present work using simple surfactant-free hydrothermal method. XRD peak of the film 5B observed at $\sim 33^\circ$ (2θ) represents the (104) $^\#$ plane of Ti_2O_3 titanium sub-oxide (JCPDS card no. 89-4746) and the remaining XRD peaks correspond to rutile TiO_2 phase (JCPDS card no. 88-1175) with intense peak of (101) plane. The GT of 150°C reduced the Magneli

Figure 1. XRD patterns of hydrothermally grown titanium oxide films: (a) 2A, 2B and 2C and (b) 5A, 5B and 5C.

phase of Ti_4O_7 obtained at GT 120°C and formed the mixed phases of $\text{TiO}_2 + \text{Ti}_2\text{O}_3$ from the 3 M HCl added precursor solution. Zhong *et al* [19] also reported the formation of novel $\text{TiO}_2 + \text{Ti}_2\text{O}_3$ composite nanorod arrays possessing potential application for lithium ion batteries. The XRD pattern of the film 5C (GT 180°C; 3 M HCl) confirms the formation of pure rutile tetragonal TiO_2 phase with intense XRD peak of (110) plane (JCPDS data: 88-1175). The GT and HCl concentration in the precursor solution is very important for the crystallization and phase transformation of titanium oxide. Nadzirah *et al* [28] reported that the increment of temperature when HCl stabilizer was used, the TiO_2 transformed from anatase phase to rutile phase due to the thermally promoted crystallite growth. In the present work, the increment of GT from 120 to 180°C promoted the crystallite growth in the HCl added precursor solution medium. Hence, the formation of Ti_4O_7 Magneli phase is observed at low GT at 120°C (5A), whereas an increment of GT at 180°C (5C) yielded the stable rutile TiO_2 phase.

The crystallite size was calculated using the Scherrer formula [29] and interplanar spacing (d) was estimated from the preferential growth peak of the films 2A, 2B, 2C, 5A, 5B and 5C and they are compared to the corresponding standard values in table 1. Further, table 1 gives the film thickness estimated from the gravimetric method. The results presented in table 1 evidently show the influence of GT and HCl concentration in the precursor solution in the formation of different phases of titanium oxide.

3.2 Morphological properties

The morphological features of the hydrothermally synthesized titanium oxide films were investigated using SEM and the images are shown in figures 2 and 3. Generally, hydrothermal process is proven to be an efficient method for growing inorganic materials from the supercritical state of solution achieved through heating the solution which increases the pressure and thus, the hydrothermal process results in the formation of nanostructured particles [30–34]. During the hydrothermal growth process, the solution becomes supercritical and facilitates the development of various microstructured titanium oxides on the seed layer. SEM images of the hydrothermally grown TiO_2 film 2A at GT of 120°C are given in figure 2a–c, which show the coral reef arrangement of microstructures (diameter = ~ 1.6 – $1.8 \mu\text{m}$) over titanium oxide seed-layered glass substrate. These microstructures are developed from the agglomerated small nanoparticles created from the supercritical solution under ambient conditions. SEM image of the microstructures given in figure 2c resembles the natural image of coral reef structure shown in figure 2d. Increasing the GT to 150°C (film 2B) has led to the formation of cauliflower-like TiO_2 structures (diameter = ~ 1.7 – $2 \mu\text{m}$), which are shown in figure 2e–g. The structures shown in figure 2g compare well with the natural cauliflower image given in figure 2h. Increasing the GT to 180°C (film 2C) yielded multi-petals flower-like microstructures (diameter = ~ 1.4 – $2.1 \mu\text{m}$) with

Table 1. Comparison of structural parameters of titanium oxide microstructure films prepared from 1 M HCl (films 2A, 2B and 2C) and 3 M HCl (films 5A, 5B and 5C) added precursor solution at GTs of 120, 150 and 180°C.

Film	JCPDS card no.	Phase	$(h\ k\ l)$	Standard d (Å) (JCPDS data)	Present work			
					Calculated d (Å)	Crystallite size (nm)	Thickness (μm)	Band gap (eV)
2A	88-1175	Rutile TiO_2	(110)	3.194	3.328	18	1.2 ± 0.2	2.99
2B	88-1175	Rutile TiO_2	(110)	3.194	3.260	19	1.55 ± 0.2	2.96
2C	88-1175	Rutile TiO_2	(110)	3.194	3.183	23	2 ± 0.2	3.02
5A	72-1724	Ti_4O_7	(10 $\bar{2}$)	4.276	4.105	15	2.3 ± 0.2	2.93
5B	88-1175 + 89-4746	$\text{TiO}_2 + \text{Ti}_2\text{O}_3$	(101)	3.194	3.188	24	2.5 ± 0.2	2.90
5C	88-1175	Rutile TiO_2	(110)	3.194	3.183	12	3.2 ± 0.2	2.96

Figure 2. SEM images: (a–c) film 2A; (e–g) film 2B; (i–k) film 2C; (d) natural image of coral reef, (h) cauliflower and (l) multileaves flower.

increase in the number of flowers shown in figure 2i–k. The SEM image (figure 2k) resembles that of a natural flower structure (figure 2l). The SEM image results of films 2A, 2B and 2C show the development and transformation of titanium oxide microstructures due to increase in GT. In the present work, ‘dissolution and recrystallization mechanism’ [34] plays a crucial role in modifying the morphology of titanium oxide microstructures from coral reef to flower-shaped microstructures via cauliflower structures; thus the GT of hydrothermal process triggered the dissolution

and recrystallization mechanisms. Also, increase in the GT of the hydrothermal process modifies the supersaturation level of the solution and the pressure [29]. Hence, the number of nucleation sites is increased with increase in GT from 120 to 150°C [6]. Hence, the coral reef-shaped structures obtained at GT 120°C (film 2A: figure 2a–c) is modified like a cauliflower structure at GT 150°C (film 2B: figure 2e–g). Further increase in GT to 180°C, resulted in the well-separated multileaves flower-shaped structures (figure 2i–k).

Figure 3. SEM images of hydrothermally grown titanium oxide microstructures from 3 M HCl added precursor solution at GT 120°C: (a–c) (film 5A), GT 150°C; (d–f) (film 5B) and GT 180°C and (g–i) (film 5C).

The SEM images of the films prepared by adding 3 M HCl in the precursor solution at three different GTs are shown in figure 3a–i. SEM images presented in figure 3a–c show that the surface of Ti_4O_7 film (film 5A) contains agglomerated ball-shaped structures attached with nanorods over titanium oxide-seeded glass substrates. The SEM images of film 5B containing mixed phase of $\text{TiO}_2 + \text{Ti}_2\text{O}_3$ are shown in figure 3d–f, which resulted in the formation of cactus-like microstructures over titanium oxide-seeded glass substrates. In this work, the reason behind the modification of morphology may be due to the increase in the nucleation sites. The increase in GT from 120 to 150°C modifies the supersaturation level of hydrothermal solution and the pressure, hence the nucleation sites are increased in the hydrothermal process [6]. Therefore, due to the presence of high nucleation, the agglomerated ball-shaped nanorod morphology is changed to cactus-like microstructures. The SEM images of film 5C, which contains rutile TiO_2 phase are shown in figure 3g–i. The pure rutile TiO_2 phase (film 5C) resulted in the

formation of jasmine flower-like structures and the flower's petal structures are created with the bunch of agglomerated nanorods. The increase in GT to 180°C increases the supersaturation level of hydrothermal solution, which in turn enhances the nucleation sites. Hence, the branches of cactus microstructure (figure 3d–f) started to merge together due to high nucleation and form jasmine flower-like structures (figure 3g–i).

SEM images presented in figures 2 (1 M HCl) and 3 (3 M HCl) show noticeable changes in the morphology for the same GTs. Increasing the HCl concentration in the precursor solution from 1 to 3 M, increases the $[\text{Cl}^-]$ ions. The $[\text{Cl}^-]$ ions around the titanates nuclei lead to the improvement of number and length of the branches of flower and rod-like structures of titanium oxide [35]. Hence, the number of branches, petals and rod-like structures of titanium oxide in 3 M HCl (films 5A, 5B and 5C) are relatively increased when compared with that of 1 M HCl (films 2A, 2B and 2C). Thus, it is proven that HCl concentration influences the morphology of TiO_2 .

Figure 4. UV–Visible absorption spectrum of titanium oxide films: (a) 2A, 2B and 2C and (b) 5A, 5B and 5C; the inset shows corresponding band gap energies.

3.3 Optical properties

3.3a UV–Visible spectroscopy: The prepared titanium oxide microstructure films were subjected to optical absorbance spectral studies in the wavelength range of 350–750 nm. The response in the UV region at ~ 375 nm is observed in the absorbance spectra of hydrothermally synthesized titanium oxide films (figure 4a,b). Comparing the hydrothermally synthesized films in figure 4a, the strong response in absorbance observed in the films at ~ 375 nm is decreasing in the following order: film 2C (multi-petal flower-structured rutile TiO_2) > film 2A (coral reef-structured

rutile TiO_2) > film 2B (cauliflower-structured rutile TiO_2). Similarly in figure 4b, the strong response noticed in absorbance at ~ 375 nm is decreasing in the following order: film 5B (cactus-structured $\text{TiO}_2 + \text{Ti}_2\text{O}_3$) > film 5A (agglomerated ball-shaped Ti_4O_7) > film 5C (jasmine flower-structured rutile TiO_2). Thus, the variation in absorbance at 375 nm is due to the modification in their morphology, density of microstructures and phases which agree well with the previous reports [6,20]. The absorption cut-off edge of cauliflower-structured film 2B and agglomerated ball-shaped film 5B shows the red shift to longer wavelengths comparing with the various morphologies of the films (2A, 2C, 5A and 5C) grown in the present work.

The indirect optical band gap (E_g) energy of the all synthesized films was estimated using the Tauc approach from UV–Visible absorbance spectra [36] using the relation, $\alpha h\nu = K(h\nu - E_g)^n$, where α is the absorption coefficient; α is calculated from the relation $\alpha = 2.303A/d$, here d is the film thickness and A is the measured absorbance. K is a constant, $h\nu$ is the photon energy, the exponent ‘ n ’ depends on the nature of transition. For direct allowed transition, $n = 1/2$ and for indirect allowed transition, $n = 2$. The indirect optical band gap energy of TiO_2 films was obtained by extrapolating the linear portion of the plot to the x -axis. The inset of figure 4a,b reveals that the E_g of the synthesized titanium oxide films is in the range of 2.90–3.02 eV. The observed change in band gap energy is due to the change in the crystallite size [37] and phase of titanium oxide films (table 1).

3.3b PL study: The room temperature PL spectra of the prepared TiO_2 microstructure films recorded for the excitation frequency at 380 nm are given in figure 5a,b. Six main emission peaks are observed at 405, 420, 465, 485 and 585 nm for the microstructured TiO_2 films. The first emission peak at 405 nm is obtained due to the direct transition from the conduction band to valence band [38]. The emission peaks around 420, 485 and 518 nm are observed due to the defect centres formation along with the oxygen vacancy [39]. The previous works confirm the characteristic emission peak of rutile phase TiO_2 at ~ 466 nm [38,40]. In the present work, the characteristic emission peak of rutile phase TiO_2 observed at 465 nm in all the rutile phase TiO_2 microstructured films (2A, 2B, 2C, 5B and 5C). The characteristic emission peak (465 nm) of rutile TiO_2 disappeared in the Magneli phase of Ti_4O_7 (film 5A). Thus, the PL results evidently show the absence of rutile phase in film 5A (Ti_4O_7). Figure 5(a) shows decrement in PL emission peak intensity, thus confirming the lower recombination rate of electron–hole pairs in films 2A, 2B and 2C (1 M HCl) due to the increase of GTs from 120 to 180°C. The films 5A, 5B and 5C (3 M HCl) show the increment in emission peak intensity when increasing the GT from 120 to 180°C, because of the presence of various phases in titanium oxide films (figure 5b).

Figure 5. PL spectrum of titanium oxide films: (a) 2A, 2B and 2C and (b) 5A, 5B and 5C.

4. Conclusions

A simple surfactant-free hydrothermal method is shown to be potential to grow pure rutile TiO_2 and titanium sub-oxide microstructure over titanium oxide-seeded glass substrates. The HCl concentrations in the precursor solution and GTs have effectively modified the crystalline properties and growth of microstructures. The XRD studies reveal that the 1 M HCl added precursor solution form the pure rutile TiO_2 microstructures at the GTs of 120, 150 and 180°C and the crystallinity is improved with an increase in GT. Titanium sub-oxides of Ti_4O_7 , $\text{TiO}_2 + \text{Ti}_2\text{O}_3$ phase films are formed from the precursor solution containing 3 M of HCl, whereas increase in GT (180°C) formed pure rutile TiO_2 . The 1 M HCl added precursor solution at the GTs of 120, 150 and 180°C formed coral reefs, cauliflower- and flower-like microstructures of pure rutile TiO_2 over titanium oxide-seeded glass substrates. Precursor solution containing 3 M HCl resulted in the agglomerated ball-shaped microstructures of Ti_4O_7 at GT 120°C and cactus-like microstructures of mixed phases of ($\text{TiO}_2 + \text{Ti}_2\text{O}_3$) at GT 150°C, whereas the GT of 180°C formed jasmine flower-like microstructured rutile TiO_2 . The indirect optical band gap of all the microstructured films of this work is ranging from 2.90 to 3.02 eV. The PL spectra revealed oxygen vacancy and defects in microstructured titanium oxide films. Thus, the concentrations of HCl (1 and 3 M) in the precursor solution along with the different GT seem to be potential in modifying the surface morphology of the films formed on the seeded glass substrates.

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