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# Synthesis of Novel Nano-Strawberry $TiO_2$ Structures with the Aid of Microwave Inverter System: Growth Time Effect on Optical Absorption Intensity

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**Abstract** A novel anatase $TiO_2$ with nanostrawberry-like structure with high porosityhas been synthesised on ITO, with the aid of microwave power in a very short duration of 6 minutes. The growth of these novel $TiO_2$ nanostructures on ITO is attained stoichiometrically by using ammonium hexafluorotitanate, Hexamethylenetetramine, and Boric acid as precursor, capping agent, and reducing agent, respectively. Optical absorption intensity and thickness of these nanostructure layers can be varied by the growth time. A highly porous, 2.25 $\mu$m thickest layer has been successfully synthesised on ITO, andthe average diameter of these nanostructures was foundapproximately 70±2.5nm. These highly porous nanostructures are expected to begood candidate for photocatlysis applications and efficient photovoltaic performances of dye sensitised solar cells.

**Keywords:** Anatase $TiO_2$nanostrawberry, Porous, Microwave assisted, Short duration, Growth time effect, Optical absorption intensity.

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## 1. Introduction

A wide range application of $TiO_2$ as a semiconductor in photocatlysis [1], sensors [2], optical devices [3], fuel cells [4], and dye sensitized solar cell [5] has made its research worthy. It exists in three mineral forms, anatase, rutile, and brookite [6]. Among these forms, anatase is preferred, due to its crystalline structure, and high photocatalytic activity, stable, non-toxic, and cheaper as well , and surface energy of anatase facets 101, 200, and 001 are 0.44 $Jm^{-2}$, 0.53 $Jm^{-2}$, 0.90 $Jm^{-2}$, respectively [6]. In recent years, a variety of synthesis methods such as hydrothermal method, solvothermal method, sol-gel method, direct oxidation method, chemical vapour deposition (CVD), electrodeposition, sonochemical method, and microwave method have been used for the preparation of $TiO_2$ nanostructured [7]. Studies has shown that growth of anatase $TiO_2$ nanostructuresincreases in reduced time, when temperatures are kepthigh, during chemical reactions in liquid phase deposition method (LPD) [8]. Microwave heating has privileges of rapidness, energy saving, and uniformity over conventional heating [9]. Thermal heating process involve conduction, convection, and radiation, which involves indirect heating, whereas in microwave heating, electromagnetic waves are directly

absorbed at the molecular level [10], which leads to save the energy and can be the reason of rapid reaction. Most important features of microwaveare to polarize the materials of high dielectric constant, and power generation in these materials due to their high dielectric loss, and hence quick and efficient heating is attained [11]. Many researchers have reported synthesis of anatase $TiO_2$, which has limited the synthesis time up to 3 hours [12-13]. In this research paper, we report synthesis of anatase $TiO_2$nanostructures assisted by 180W micro wave power in 6 minutes.

## 2. Experimental

Precursor, Amoniumhexafluorotitanate $(NH_4)_2TiF_6$, and HMT ($C_6H_{12}N_4$) were purchased from Sigma-Aldrich USA. Boric acid ($H_3BO$) from WAKO company Japan, and ITO (indium tin oxide) substrate of sheet resistance ca. 9-22 Ω,/square was purchased from VinKarola instruments USA. We have synthesized $TiO_2$nano structures on ITO assisted by microwave (inverter system). ITO substrates were dusted by high quality soft cotton, and then after they were passed through a process of ultrasonication, using acetone and 2-propanol respectively. These substrates were immersed in a solution, which contained 1.5 ml of each precursor ($NH_4TiF_6$), boric acid, and surfactant (HMT), whereas the concentration of precursor, boric acid, and surfactantwere 0.1 M, 0.06, and 0.03M. It took 6 minutes to grow $TiO_2$ nanostructure on ITO, when microwave power was set at 180 watt. For the same combination of these molarities, growth time of nano structures was increased by repeating growth cycles. These cycles were named as 1X, 2X, 3X,4X, 5X, and 6X representing growth times 6, 12, 18, 24, 30, and 36 minutes respectively. For each growth cycle, freshly prepared solution was used in new reaction bottle to avoid any residue contamination of previous reaction cycle. After these growth cycles, these substrates were rinsed with pure water in abundant and were dried with nitrogen gas. Finally, each substrate was annealed in air at 350$^o$C for an hour.

X-ray diffraction method (BRUKER D8 Advance) with CuK$\alpha$ radiation of wavelength 0.154 nm of scan step 2$^o$/min, Field Emission Scanning Electron Microscope (FESEM) technique (ZeiSS SUPRA 55VP), and UV/VIS spectrometer (Lambda 900 Perkin-Elmer) were used to carry out investigations regarding the Structure, surface morphology, and optical properties, respectively for these samples.

## 3. Results and Discussion

In order to characterise synthesised nanostructures, XRD analysis was carried out for these samples, which is shown in Figure 1. The values of '2Θ' correspondent to diffracted peaks attained from X-ray diffraction pattern of the samples are 25.20, 37.88, 48.08, 53.80, and 55.08. According to file JCPDS No.21-1272, values of '2Θ', 25.28, 37.88, 48.05, 53.89, and 55.06 are correspondent to facets 101, 004, 200, 105, and 211 respectively for $TiO_2$ anatase phase. The structure of the samples are obviously in anatase phase, because the diffraction peaks attained for the samples at '2Θ' strongly match with the results of JCPCDS card No.21-1272, and their high exposure

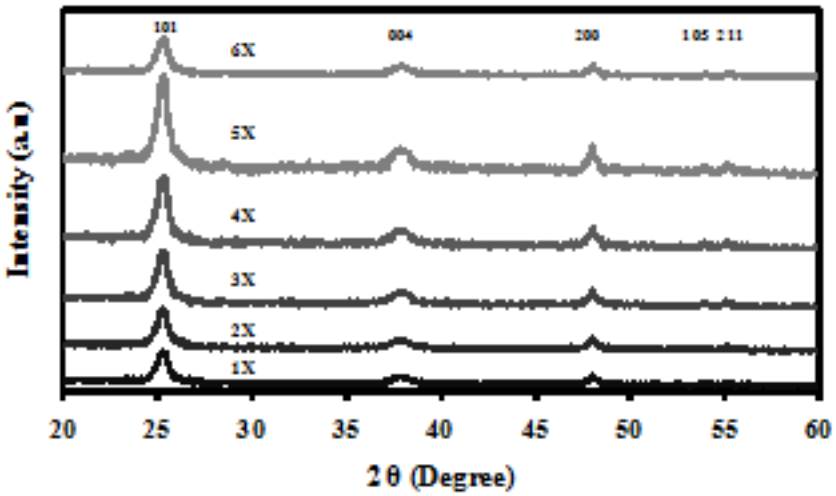


**Figure** 1: XRD diffracted peaks of novel $TiO_2$ nanostrawberry structures at 2Θ (degree), 25.28, 37.88, 48.05, 53.89, and 55.06 match with anatase facets 101, 004, 200, 105, and 211, respectively, when growth time was set for 1X-6X cycles.

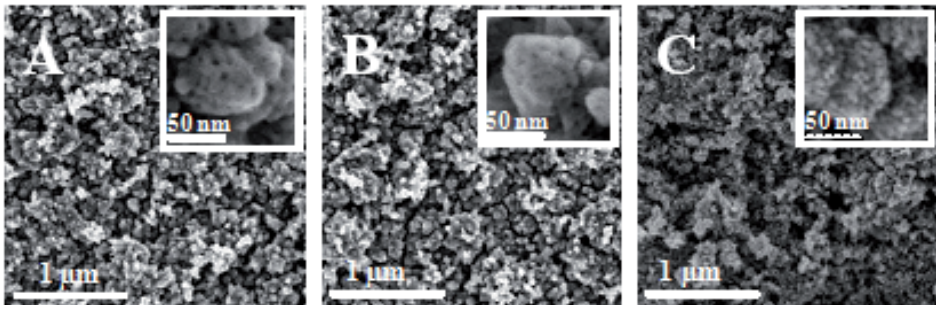


**Figure** 2: Low resolution FESEM images of homogeneous growth of novel $TiO_2$ nanostrawberry structures and (b)-Inset, high resolution FESEM images showing the effect (size and porosity) of growth cycles: (A) 2X, (B) 5X, and (C) 6X.

of facet 101 along with unusual slightly more exposure of facet 200 confirms novel $TiO_2$ nanostructure. On analysis, it is found that for each sample, ratio of the peaks corresponding to the facet 101 to facet 200 is (0.08, 0.083, 0.11, 0.12, 0.20, and 0.47 respectively for 1X-6X) increasing, which depicts increasing exposure of facet 200 with respect to facet 101 as the growth time is increased. It is also observed that position of the peaks does not change, whereas the intensity of the peaks increases with increase in growth time. It portrays that growth time has affected the quantity, and orientation of anatase phase $TiO_2$ nanostructures

A unique $TiO_2$ nanostructuredepicted from XRD analysis was verified by low and high resolution images of the samples attained by using FESEM facility. A very homogeneous growth of highly porous, like nanostrawberry structureson ITO can be seen in fig.2.

It is observed that after first growth cycle average diameter of $TiO_2$nanostrawberries is 60± 5nm, and after second growth cycle some porosity is seen on the surface of $TiO_2$ nanostrawberry structures, which is shown in inset fig. 2-A. For further growth cycles, porosity is increased to a great extent, whereas size of $TiO_2$ nanostrawberry structures

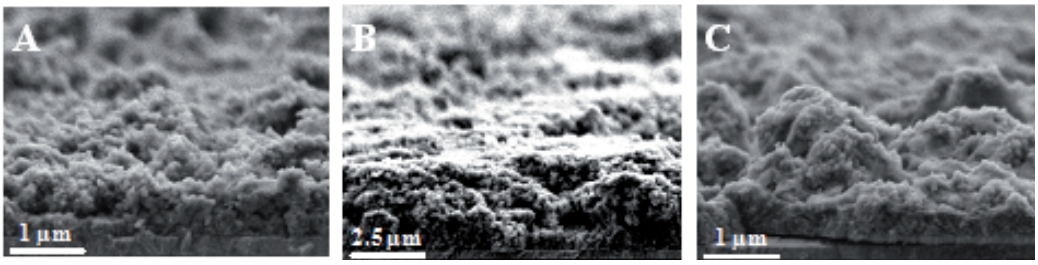


**Figure** 3: FESEM images; Effect of growth cycles on thickness of $TiO_2$ layers. Samples (A) 2X, (B) 5X, and(C) 6Xof thickness 658 nm, 2.25 $\mu$m, and 547 nm respectively.

are slightly increased, which are shown in high resolution FESEM images in inset fig. 2.B-C.

The mechanism of formation of anatase $TiO_2$ like nanostrawberry structure is based on use of hexamethylenetetramine as decoupling between hydrolysis and polycondensation of Ti-ions and $NH_3$. Hydrolysis of hexamethylenetetramine ($C_6H_{12}N_4$) produces $NH_3$ and $OH^{--}$, and further hydrolysis of ammonium ($NH_3$) produces $NH_4$ and $OH^-$. Hydrolysis of ammonium hexafluorotitanate produces $NH_4^+$ and $(TiF_6)^{2-}$. Further hydrolysis of $(TiF_6)^{2-}$ produces $Ti^{4+}$, $Ti(OH)_6^{2-}$, and fluorine ions. The predicted reaction, $Ti(OH)_6^{2-} \rightleftarrows TiO_2 + 2H_2O + (OH)^{--}$ does not show stability. Here terminated fluorine ions play a role to form HF by combining with hydrogen ions released from hydrolysis of boric acid. The synergetic effect of HF and HMT leads to produce unique anatase $TiO_2$ like nanostrawberry structure. Microwave power has provided sufficient energy to these ions to react more efficiently. Hence the active solvation and particularbonding effect of capping agents lead to produce porous $TiO_2$ nano structures with exposed facets [101], and [200].

It is also observed that thickness of $TiO_2$ layer grown on ITO increases after each growth cycle, unless it reaches to its maximum, and then after the next growth cycles, it starts depleting. It is found that 280 nm, 658 nm, 691 nm, 1.65 $\mu$m, and 2.25$\mu$m thick layers are synthesised when growth time is set for 1X-5X cycles, respectively. However, after sixth cycle, $TiO_2$ layer is depleted to a great extent and just 547 nm is left on ITO. Fig. 3 shows the FESEM images of thickness of $TiO_2$ layers attained on ITO after 2 X, 5 X and 6X growth cycles. It is apparent that growth cycles (1X-5X) have not affected the morphology of $TiO_2$ nanostrawberry structures, but have increased porosity, size and layer thickness of $TiO_2$ nanostrawberry structures on ITO. Depletion in thickness after sixth cycle can be due to these factors, (a) inadequate support to large sized nanoparticles grown on the top of small sized nanoparticles with low adhesion, and (b) the decrease in compactness, which is caused by increasing porosity beyond a certain growth cycle.

Ultravoilet-visible (UV/Vis) absorption spectra analysis of these samples was carried out to scrutinize the usefulness of novel $TiO_2$ nanostrawberry structures in photochemical processes and photonics. In order to investigate the effect of growth time on optical absorption capabilities of these novel highly porous $TiO_2$nanostructures, a thickness-based normalised UV/V is absorption spectra is plotted, which is shown in fig.4. It is

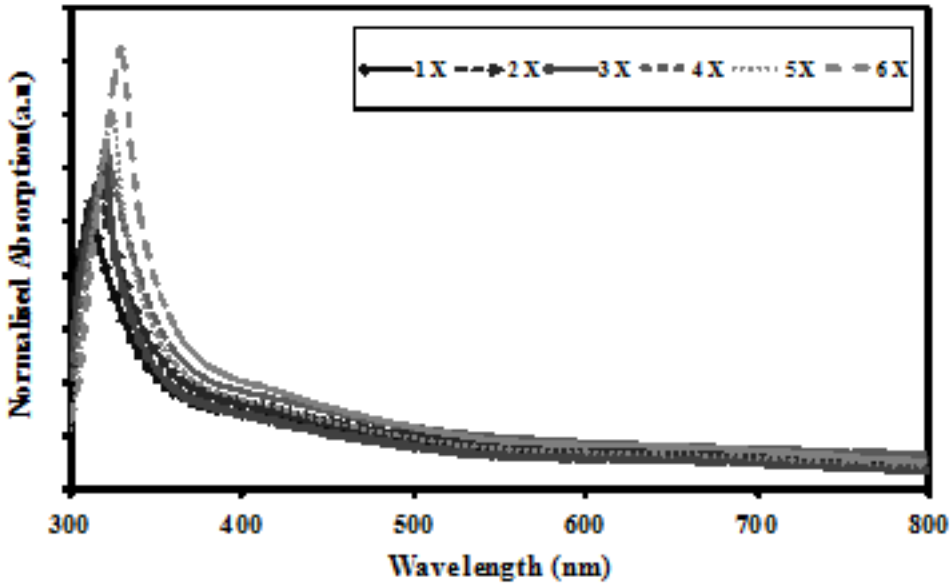


**Figure** 4: Thickness-based Normalised optical absorption spectra of $TiO_2$nanostrawberry structures for the growth cycles 1X-6X. Red shift is observed for higher growth cycles.

observed that absorption level increases by increasing the number of growth cycles (1X-6X), and their optimum absorption is at wavelength 320±10 nm approximately.

Matching these results with figures 2, and 3, strengthen that optical absorption level is directly proportional to porosity, which has shown its dependence on growth time. The increasing trend in absorption level is also shared by hickness, which is mounting hereover 1X-5X. If this rise in intensity has its prominentshare due to the porosity of nanostructures then absorption level should still be rising even when it is judged for standard normalised thickness. Fig. 4 reveals this fact for the samples 1X-6X, even though the thickness of sample6Xis reduced but has shown its highest normalised absorption intensity level forhighly porous structure. A slight red shift in wavelength of 20 nm corresponding to optimum absorption is observed by increasing growth cycles 1X-6X, which indicates lowering down of band gap in these nanostructures, which should be due to exposure of the surface containing high electron density, and XRD analysis also advocates that increasing exposure of high energy facet 200 is because of increase in growth time.

## 4. Conclusion

In conclusion, a novel porous nanostrawberry anatase $TiO_2$ structure has been successfully synthesised on ITO, with the aid of microwave power in a very short duration. Porosity of these nanostructure layers can be increased by varying the growth time. So far 2.25 $\mu$m optimised thick layer can be deposited on ITO, and the average diameter of these highly porous nanostructures is 70±2.5 nm. It is found that growth time has its encouraging effect on optical absorption intensity. Due to its high absorption at 320±10 nm wavelength, these highly porous anatase phase $TiO_2$ like nanostrawberry structures can be helpful to enhance photocatalytic processes, and can be used to

enhance photon-current efficiency of dye sensitised solar cells as well, when applied as a photo-electrode.

## References

[1] S. K. M. Saad, et al., Porous (001)-faceted Zn-doped anatase TiO2 nanowalls and their heterogeneous photocatalytic characterization, *RSC Advances*, **4**, 57054–57063, (2014).

[2] J. Nisar, Z. Topalian, A. De Sarkar, L. Österlund, and R. Ahuja, TiO2-based gas sensor: a possible application to SO2, *ACS Appl Mater Interfaces*, **5**, 8516–8522, (2013).

[3] A. F. Khan, M. Mehmood, T. Ali, and H. Fayaz, Structural and optical studies of nanostructured TiO2–Ge multi-layer thin films, *Thin Solid Films*, **536**, 220–228, (2013).

[4] J. Tang, J. R. Durrant, and D. R. Klug, Mechanism of photocatalytic water splitting in TiO2. Reaction of water with photoholes, importance of charge carrier dynamics, and evidence for four-hole chemistry, *J Am Chem Soc*, **130**, 13885–13891, (2008).

[5] A. A. Umar, S. Nafisah, S. KM. Saad, S. T. Tan, A. Balouch, M. M. Salleh, and M. Oyama, Poriferous microtablet of anatase TiO2 growth on an ITO surface for high-efficiency dye-sensitized solar cells, *Sol Energy Mater Sol Cells*, **122**, 174–182, (2014).

[6] M. Lazzeri, A. Vittadini, and A. Selloni, Structure and energetics of stoichiometric TiO2 anatase surfaces., *Physical Review B*, **36**, no. 15, (2001).

[7] M. M. Byranvand, et al., A Review On Synthesis Of Nano-TiO2 Via Different Methods, *Journal of Nanostructures*, 1–9, (2013).

[8] A. A. Umar, M. Y. A. Rahman, S. K. M. Saad, M. M. Salleh, and M. Oyama, Preparation of grass-like TiO2 nanostructure thin films: effect of growth temperature, *Appl Surf Sci*, **270**, 109–114, (2013).

[9] Y. U. Bykov, K. I. Rybakov, and V. E. Semenov, High-temperature microwave processing of materials, *Journal of Physics D: Applied Physics*, **34**, no. 13, p. R55, (2001).

[10] E. T. Thostenson and T.-W. Chou, Microwave processing: fundamentals and applications, *Compos, Part A Appl Sci Manuf*, **30**, 1055–1071, (1999).

[11] A. A. Salema, Y. K. Yeow, K. Ishaque, F. N. Ani, M. T. Afzal, and A. Hassan, Dielectric properties and microwave heating of oil palm biomass and biochar, *Ind Crops Prod*, **50**, 366–374, (2013).

[12] Y. Tao, C.-Y. Wu, and D. W. Mazyck, Microwave-assisted preparation of TiO2/activated carbon composite photocatalyst for removal of methanol in humid air streams, *Ind Eng Chem Res*, **45**, 5110–5116, (2006).

[13] B. S. Shirke, P. V. Korake, P. P. Hankare, S. R. Bamane, and K. M. Garadkar, Synthesis and characterization of pure anatase TiO2 nanoparticles, *J Mater Sci Mater Electron*, **22**, 821–824, (2011).