

Synthesis and Characterization of Highly Crystalline Anatase Titania

A Dissertation Submitted in partial fulfilment
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CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis and Characterization of Highly Crystalline Anatase Titania**” being submitted by Dayanidhi Mohanta to the Department of Chemistry, National Institute of Technology, Rourkela, for the award of the degree of Master of Science is a research carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the dissertation has not been submitted to any other University/Institute for the award of any Degree/Diploma.

N.I.T, Rourkela

Date:

Dr. Aparna Mondal
(Supervisor)

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Rourkela

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ABSTRACT

Samarium (Sm) doped titania samples were prepared through sol-gel process by using titanium oxosulphate as precursor for titanium and samarium oxide as a precursor for Sm^{3+} ions. The main objective of the proposed study is to stabilize the anatase phase of titania up to high temperatures. Thermal analysis showed a weight loss of 21 % on heating up to 1000°C in an inert atmosphere. IR analysis showed the complete removal of the surfactant on calcination at 500°C for 2 h. The obtained samples were characterized by X-ray diffraction XRD, SEM, UV, TG-DTA & FTIR studies. It was found that the anatase phase of titania was stable up to 850°C . The catalyst showed visible light absorption as evident from the UV-VIS spectrum and was found to be an active photo catalyst in sunlight.

CHAPTER-I

INTRODUCTION

Titania powders have wide spread use as pigments because of their high light scattering ability with almost no absorbance in the visible region. Titania is also used to a large extent in plastics, cosmetics, catalysts, ceramic membranes and many other applications.^{1,3} Titania has three crystallographic forms: anatase, rutile, and brookite.² Rutile TiO_2 shows higher refractive index, UV absorption and stronger mechanical durability resistance than other forms of titania, also the most thermo-chemically stable phase, so this crystal structure is preferred for high UV absorption and is typically formed at higher reaction temperatures than the anatase phase.

The anatase polymorph exhibits the highest photocatalytic activity of the three polymorphs⁴. The performance of TiO_2 in certain technical applications is strongly influenced its crystalline structure, morphology and particle size TiO_2 degradation of several environmental contaminants under UV irradiation⁵. Anatase powder with a high surface area, high degree of crystallinity, large crystallite size is desirable to enhance the photocatalytic activity, since such a powder will have relatively few disruptions in its electronic band structure⁶. Photocatalytic degradation results in the demineralization of organic matter into carbon dioxide, water and mineral acids⁷.

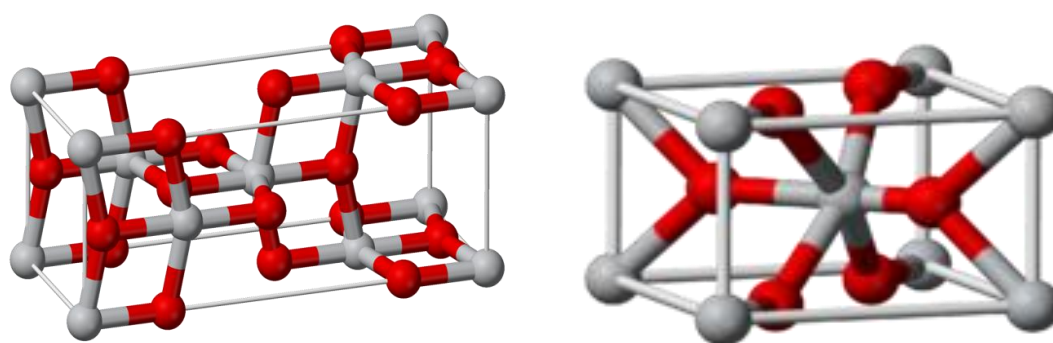


Fig. 1. Crystal structure of (a) anatase and (b) rutile titania.

The photocatalytic degradation efficiency on the surface of TiO_2 particles is still low, because of the fast recombination rate of photogenerated electron-hole pairs⁸. In order to slow down the electron-hole pairs and enhance interfacial charge-transfer efficiency, several approaches have been proposed, including transition metals doping⁹⁻¹⁰, coupled semiconductor systems¹¹⁻¹², noble metals deposition¹³ and rare earth ions doping¹⁴⁻¹⁷.

CHAPTER-II

EXPERIMENTAL PROCEDURES & MEASUREMENTS

2.1. Objective of Present Work

- Synthesis of nanocrystalline $\text{Sm}^{+3} - \text{TiO}_2$ powder form using inorganic salts and dodecylamine (DDA) as surfactant.
- Study the effect of Sm^{+3} addition on crystallite size of $\text{Sm}^{+3} - \text{TiO}_2$, and
- Structural characterization using XRD, SEM, UV, TG-DSC & FTIR studies.

2.2. Synthesis Procedures

This chapter deals with a brief discussion of synthesis procedures of $\text{Sm}^{+3} - \text{TiO}_2$ powders. Titanium oxosulphate is used as the source of titania and samarium oxide as the source of samarium. Separate solutions of both these compounds are prepared in water. These two solutions are mixed with stirring. DDA solution was added slowly with vigorous stirring. The obtained solution was stirred and NH_4OH solution was added to get a precipitate. Then the precipitate was washed with distilled water to make it chlorine free. It was then filtered and washed, dried on the water bath and powdered. The powder was calcined at different temperatures. Similar process was followed to prepare samples without surfactant.

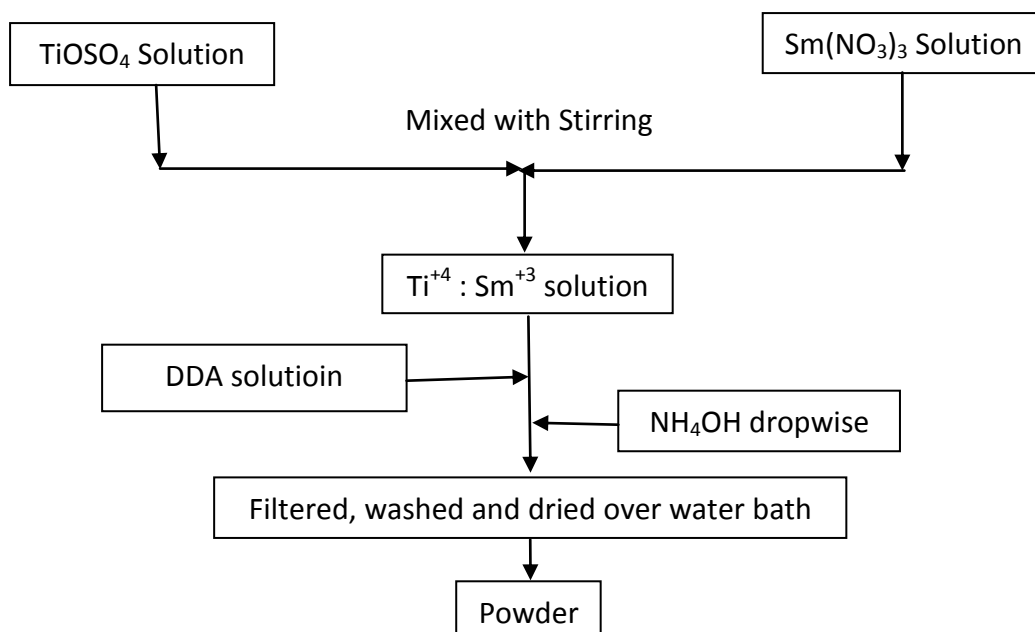


Fig. 2.1. Schematic diagram for synthesis of Sm^{+3} doped TiO_2 powder.

2.3. Characterization

X-Ray Diffraction

X-Ray Diffraction is used to perform phase analysis. The sample for this measurement was prepared by using a glass slide with a groove as the sample holder. The powder was placed in the groove and was compressed with the help of another glass slide. The excess powder was removed.

The sample at the flat surface at the slide was used to measure its characteristics X-ray diffraction pattern by using X-Ray diffractometer with the following set up,

Target	- CuK α of wavelength $\lambda = 0.1540$ nm
Range of diffraction angle(2θ)	-(20° - 80°)
Scanning speed	- 2° /min

For a crystalline solid, the structure may be specific in terms of crystal unit cell and translations symmetry, the lattice leading to sharp Bragg peaks which are characteristic of the diffraction pattern of the crystalline solids. The structure of the amorphous solid, on the other hand, is characterized by a lack of symmetry, periodicity and long range order, resulting in a diffraction pattern. By using the XRD plot and Bragg's law the peaks were identified and subsequently phases were identified. Average crystallite size in the sample has been calculated from widths $\Delta 2\theta_{1/2}$ in characteristic diffraction peaks with the Debye –Scherrer's formula, $D = 0.89\lambda / [(\Delta 2\theta_{1/2})\cos\theta_B]$, where $2\theta_B$ is the peak position in diffractogram.

Thermal and thermogravimetric analysis

Thermal decomposition/combustion of precursor mass into a dried TiO₂ ceramic powder is studied with thermogravimetry and differential scanning calorimetric analysis (TG-DSC). The data are obtained by heating the sample at 20°C/min. The measurement is done by heating the specimen at a given heating rate in nitrogen atmosphere. The peak positions in TG-DSC curve determine thermal decomposition and phase transformation or phase transition temperatures in precursor.

IR spectra

The IR spectrum was measured in the 400 to 4000 cm⁻¹ region for sample dispersed in KBr pellets (in 10:90 ratio) with IR spectrophotometer. The reported values of frequencies are accurate to ± 2 cm⁻¹ in the case of the sharp bands and ± 5 cm⁻¹ or even larger in the case of the broad bands.

SEM

SEM measurements were carried out to investigate the detailed morphology, surface roughness and structure of the powders.

CHAPTER-III

RESULTS AND DISCUSSION

3.1. DSC-TG

From the DSC-TG analysis (Fig. 3.1), we can see that there is a mass loss of ~ 17% and majority of it occurs within 200°C indicating the presence of adsorbed water molecules. The exothermic peak at 547°C corresponds to the crystallisation of titania. The presence of an endothermic peak shows the desorption of water molecules from the titania. Another exothermic peak around 1000°C is due to the anatase to rutile phase transformation.

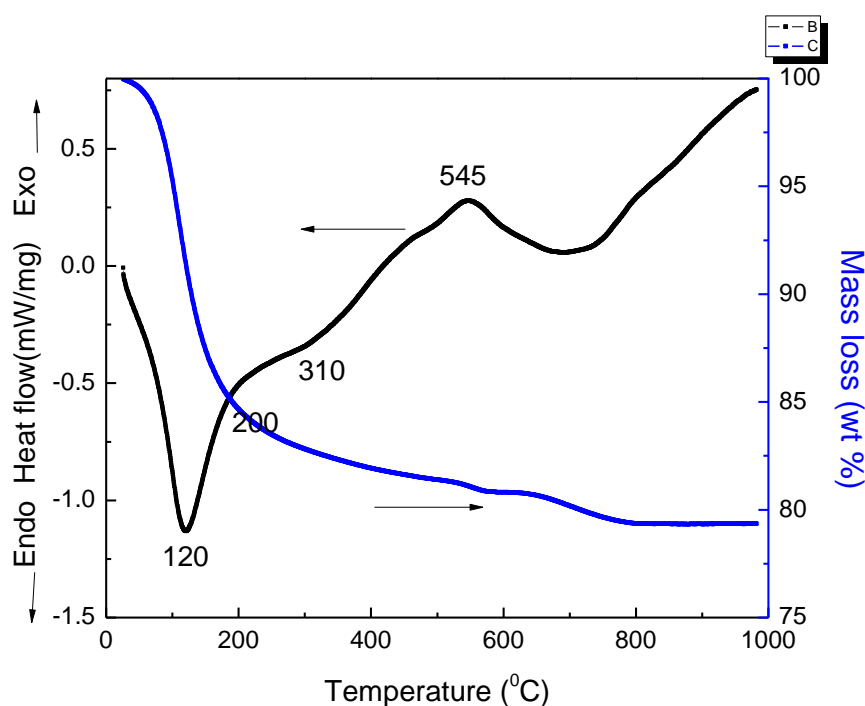


Fig. 3.1. (a) DSC plot of TiO_2 as prepared sample (b) TG plot of TiO_2 as prepared sample.

3.2. X-ray diffraction study

Figure 3.2 shows the X-ray diffractograms of pure TiO_2 prepared with and without surfactant and heated at 500°C. It shows single phase anatase structure. All the reflections of titania, which is corresponding to the anatase structure, are observed. Sample with surfactant has broad peaks than that of without surfactant, as shown in Fig. 3.3. This indicates that the sample with surfactant has smaller crystallite size than the samples prepared without surfactant.

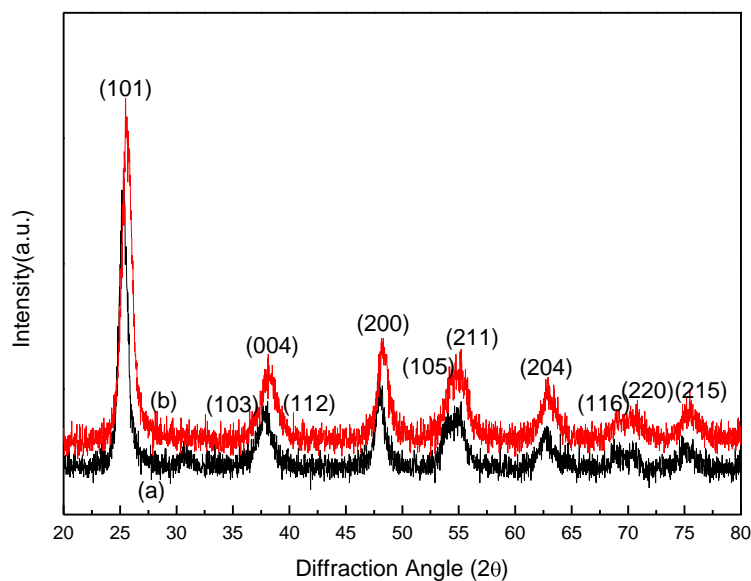


Fig. 3.2. XRD of (a) TiO₂ and (b) TiO₂-DDA calcined at 500°C.

Figure 3.3 shows the X-ray diffractograms of p-TiO₂ prepared without the DDA surfactant and heated at 500°C. The peaks show that it has single phase anatase structure. No peak corresponding to Sm⁺³ arises up to temperature as high as 850°C. It has been observed that the peak broadening of (101) decreases on increasing the calcination temperature. So, calcination temperature plays an important role in controlling the crystallite size of TiO₂.

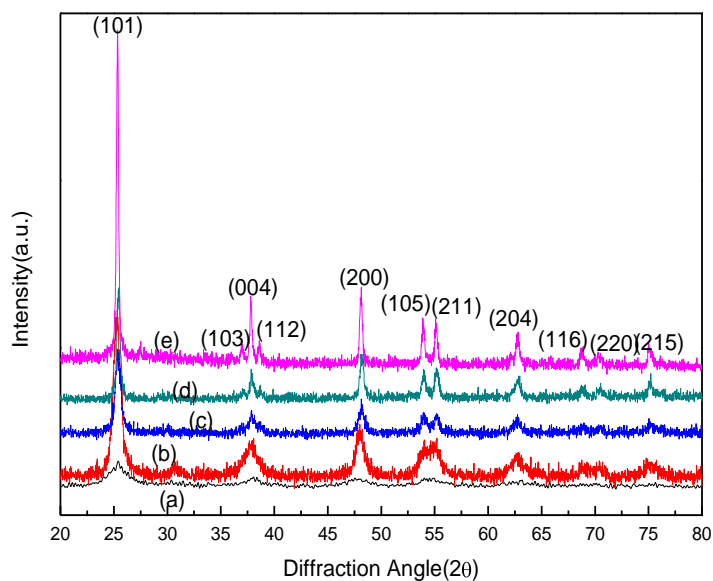


Fig. 3.3. XRD of (a) as prepared sample and samples calcined at (b) 500°C, (c) 650°C, (d) 750°C, and (e) 850°C.

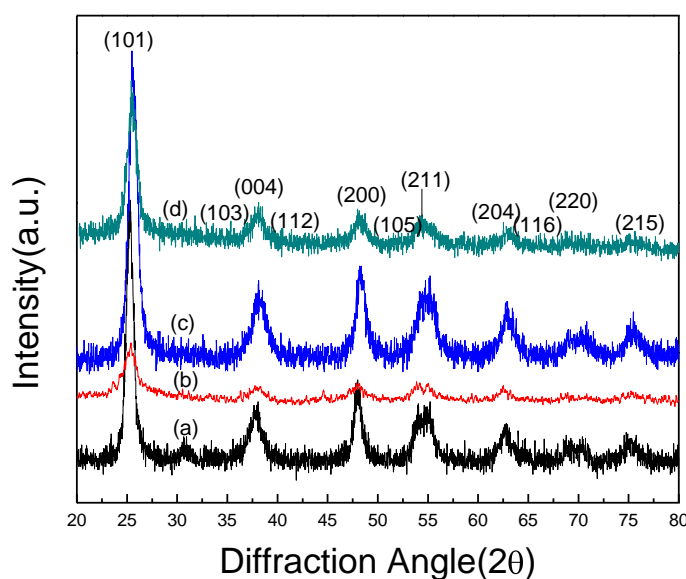


Fig. 3.4. XRD of (a) TiO_2 , (b) 0.5 SmTiO_2 , (c) 1.0 SmTiO_2 , and (d) 2.0 SmTiO_2 calcined at 500°C .

Figure 3.4 shows the X-ray diffractograms of 0.5, 1.0 and 2.0 mol% Sm^{+3} doped TiO_2 prepared without DDA surfactant and heated at 500°C . The peak shows that it has single phase anatase structure. No peak corresponding to Sm^{+3} arises up to as high content as 2.0 mol%. It been observed that the peak broadening of (101) increases on increasing the Sm^{+3} content in TiO_2 . So, Sm^{+3} plays important role in controlling the crystallite size of TiO_2 .

3.2. IR spectroscopic study

Figure 3.5 and 3.6 show IR spectra of as prepared TiO_2 and the samples heated at 500°C , synthesized with and without DDA. Peaks at 2923 and 2852 cm^{-1} correspond to the C-H stretching of hydrocarbon bonds of DDA, which are very weak in as prepared sample. The peaks related to organic compounds are very weak in the TiO_2 powders calcined at 500°C for 2 h. The results show that calcined samples are almost free from organic impurity. The broad band corresponding to $-\text{OH}$ stretching recorded in the 3000 to 3500 cm^{-1} range. For as prepared sample, the peaks around 3317 cm^{-1} and 1630 cm^{-1} correspond to the O-H stretching and bending vibrations. For the calcined samples, the peak intensity is decreased compared to as prepared sample. The results demonstrate here that the calcined sample has adsorbed H_2O molecules on the surface of TiO_2 . The peak at 1509 cm^{-1} in as prepared sample is due to asymmetric stretching vibration of carbonyl group. The peak at 1408 cm^{-1} is due to the symmetric stretching of carbonyl group. The weak peak at 458 cm^{-1} is due to the presence of Ti-O-Ti bond. The peaks from 800 to 400 cm^{-1} are due to the presence of Ti-O bond.

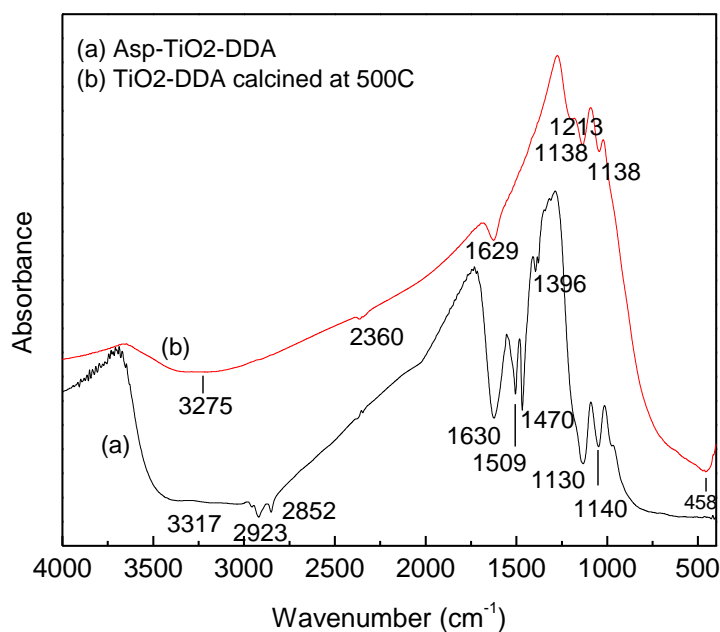


Fig. 3.5. IR spectrum of (a) as prepared TiO_2 -DDA and (b) TiO_2 -DDA calcined at 500°C .

Figure 3.6a and 3.6b show IR spectra of as prepared sample synthesized using DDA and Sm^{+3} doped TiO_2 nanopowders heated at 500°C for 2h. Peaks at 2919 and 2850 cm^{-1} correspond to the C-H stretching of hydrocarbon bonds of DDA, which are very weak in as prepared sample. The peaks related to organic compounds are very weak in the Sm^{+3} doped TiO_2 powders calcined at 500°C for 2 h. The results show that calcined samples are almost free from organic impurity. The broad band corresponding to -OH stretching recorded in the 3000 to 3500 cm^{-1} range. For as prepared sample, the peaks around 3353 cm^{-1} and 1620 cm^{-1} correspond to the O-H stretching and bending vibrations. For the calcined samples, the peak intensity is decreased compared to as prepared sample. The results demonstrate here that the calcined sample has adsorbed H_2O molecules on the surface of Sm^{+3} doped TiO_2 . The peak at 1503 cm^{-1} in as prepared sample is due to asymmetric stretching vibration of carbonyl group. The peak at 1335 cm^{-1} is due to the symmetric stretching of carbonyl group. The weak peak at 965 cm^{-1} is due to the presence of Ti-O-Sm bond. The peaks from 800 to 400 cm^{-1} are due to the presence of Ti-O bond.

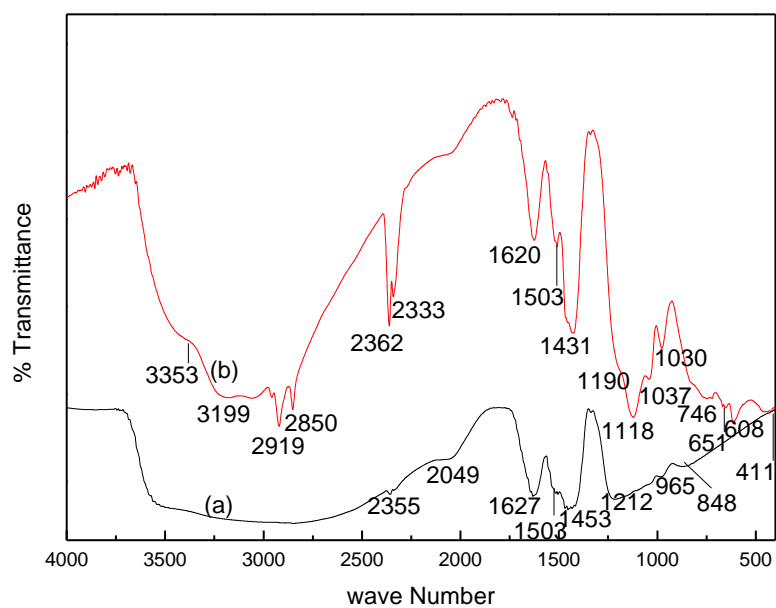


Fig. 3.6. FT-IR spectrum of (a) 0.5SmTiO_2 calcined at 500°C and (b) $0.5\text{SmTiO}_2\text{-DDA}$ calcined at 500°C

3.3. SEM

From the SEM images in Fig. 3.7., it is clear that the prepared material is not much agglomerated. The particles are not visible clearly. Not much information can be obtained from these images. It requires further investigation by transmission electron microscopy.

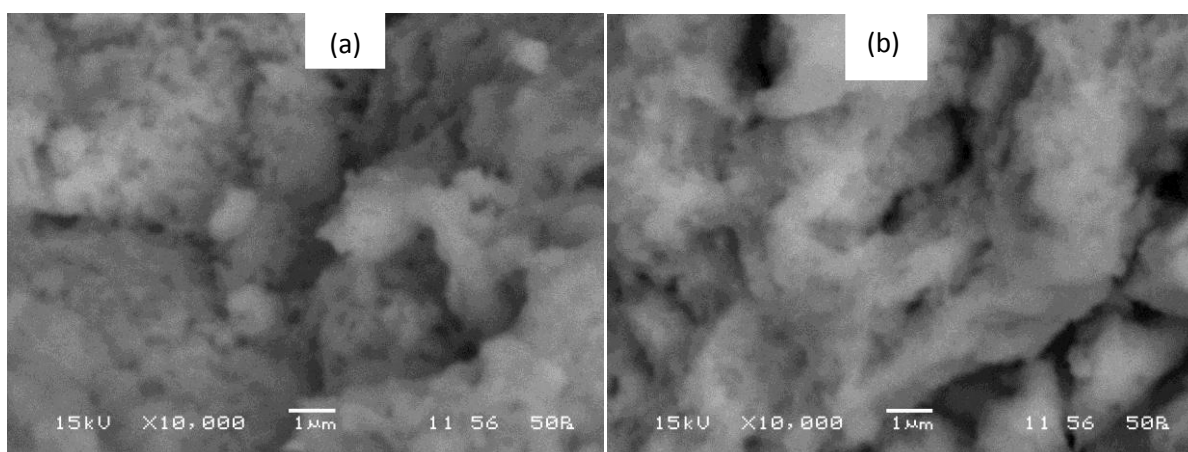


Fig. 3.7. SEM images of (a) 0.5SmTiO_2 and (b) $0.5\text{SmTiO}_2\text{-DDA}$ powder calcined at 500°C .

CHAPTER V

SUMMARY AND CONCLUSION

1. XRD analysis shows that the highly crystalline anatase phase is stabilized up to 850°C.
2. Samarium plays important role in stabilizing the anatase phase up to higher temperatures compared to the pure titania.
3. With increasing the calcination temperatures, the crystallite size of TiO₂ increases.
4. Complete removal of the surfactant (DDA) on calcination at 500°C.
5. Pure TiO₂ shows good photocatalytic activity in comparison to the Sm³⁺ doped TiO₂.

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