Chapter 4

Titanium Dioxide

4.1 Introduction

TiO_2 was synthesized using two methods to ascertain the method which gives the best results. The phase of TiO_2 used for DSSC is Anatase. Hence, another aim of synthesizing TiO_2 was to also find out the synthesis method which gives TiO_2 in Anatase phase. Looking to these objectives, the work done has been successful.

TiO_2 is an extensively studied semiconducting material. TiO_2 can be synthesized by different synthesis routes like sol gel, precipitation, hydrothermal, solvo thermal etc. TiO_2 exists in three different crystallographic structures namely Anatase, Rutile and Brookite. It is very difficult to prepare pure single phase of TiO_2.

The morphology and surface area plays an important role in the property of materials. Hence, synthesis methods using surfactants were also employed to modify these properties.

4.2 Synthesis

In the present work, TiO_2 nanoparticles in three pure crystallographic forms (Anatase, Rutile and Brookite) have been prepared by hydrothermal and precipitation methods. A set of TiO_2 samples have been prepared by hydrothermal method using different surfactants

Titanium Isopropoxide, Titanium Tetrachloride, Isopropanol, NaOH, HNO_3, and distilled water were used as starting material. All the chemicals were of analytical grade and used as received.

Preparation of Anatase TiO_2 (Sample 1)

Anatase TiO_2 was prepared by hydrothermal method. 20 ml of Ti-isopropoxide was diluted in 5 ml of isopropanol (Solution A). Another solution was made by mixing 0.5 ml of H_2O and 0.5 ml of HNO_3 (Solution B). Solution B was added drop wise into Solution A. Then the mixture was stirred at room temperature on a magnetic stirrer. After 30 minutes alcogel was obtained. The obtained alcogel was transferred into stainless steel autoclave and kept in an oven for 24 h at 240°C. The precipitates were filtered and washed first with distilled water and then isopropanol.

Preparation of RutileTiO_2 (Sample 2)

RutileTiO_2 was prepared by precipitation method. 20 ml of titanium tetrachloride was mixed with 60 ml 0.1M NH_4OH solution. The resulting solution was stirred for 48h at room temperature. The solution turned white indicating the formation of TiO_2 nanoparticles. This solution was centrifuged to obtain the precipitates. The precipitates were washed with distilled water and dried in isopropanol at room temperature.

Preparation of Brookite TiO_2 (Sample 3)

Brookite TiO_2 was prepared by hydrothermal method. 9.36 ml of titanium isopropoxide was diluted in 90 ml distilled water. The solution was stirred for 10 minutes at room temperature. Then it was transferred into stainless steel autoclave and kept in an oven at 200°C for 2 h. The precipitates were filtered and washed with distilled water.

Preparation of TiO_2 with surfactants (Samples 4, 5, 6, 7)

The property of TiO_2 generally depends on morphology, crystallinity and surface area **[1-3]**. Surfactants play an important role to modify morphology, surface area and crystallite size. Surfactants are also known as surface modifying agents. It has been reported that crystallization of Titania in the Anatase and the Rutile phase can be retarded by surfactant-assisted sol-gel process, which results in smaller grain sizes and presumably a larger surface area **[4-7]**.

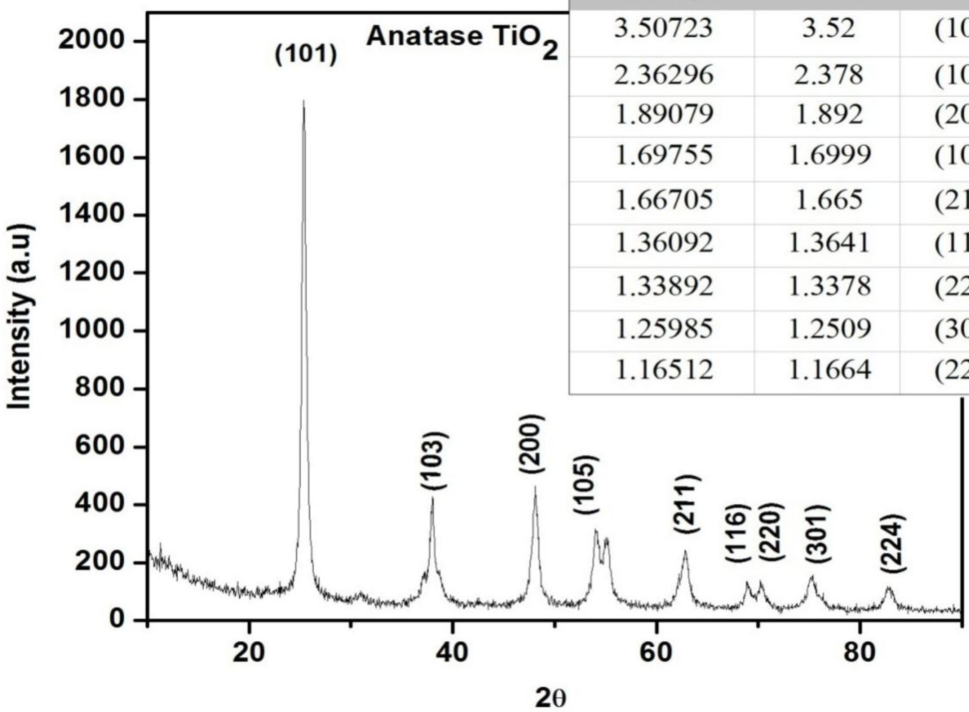
In the present work, a set of TiO_2 samples have been prepared by hydrothermal method using different surfactants like Sodium Lauryl Sulfate (SLS) *(Sample 4)*, CTAB *(Sample 5)*, Glycine *(Sample 6)* and Triton X 100 *(Sample 7)*. The surfactants were used in 2% molar ratio of TiO_2. 9.36 ml of Ti-isopropoxide was diluted in 90 ml of distilled water. Different surfactants were added at the same time. The solution was stirred for 10 minutes at room temperature. The solution was then transferred into autoclave and kept in an oven for 2h at 200°C. The precipitates were filtered and washed with distilled water. The dried samples were heated at 450°C for 4h.

4.3 Characterization

The structural properties of the samples were analyzed by X-ray diffraction (XRD). The optical properties of the prepared samples were determined by UV-Visible spectroscopy.

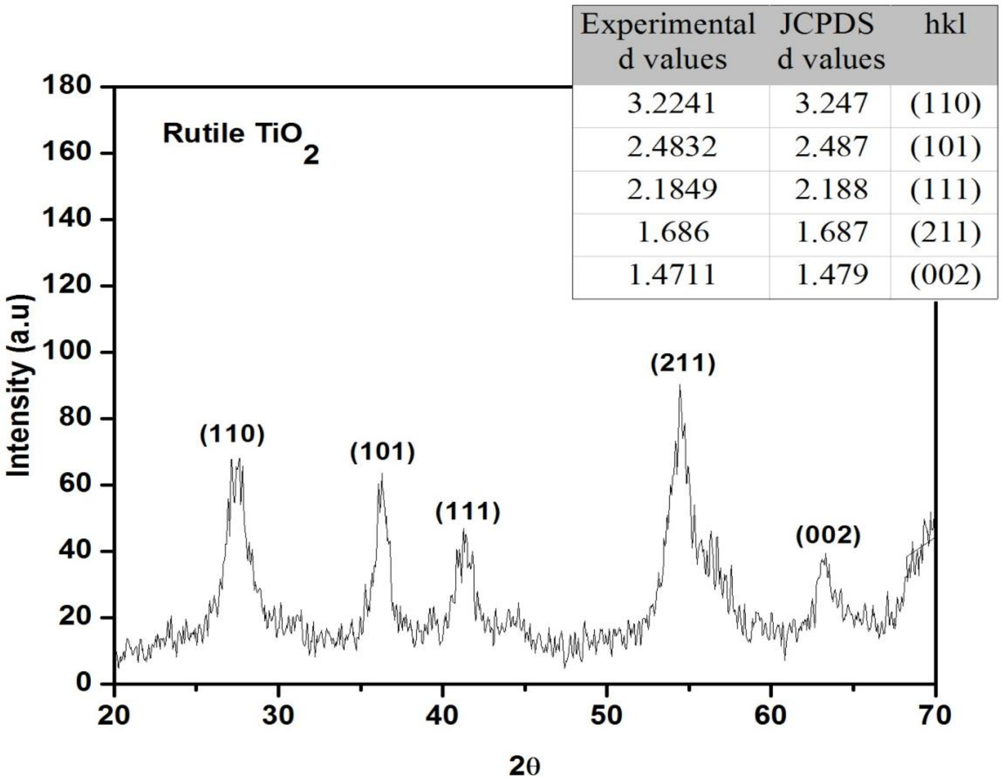
4.3.1 X – Ray Diffraction

X-ray powder diffraction of the samples was conducted at room temperature on a Bruker D8 Advance X-ray Diffractometer. The 2θ range was taken from 10° to 90° in scan mode with step increment of 0.050° and step time 2 second at room temperature. The XRD patterns of all the samples are given in Figures 1 to 7.



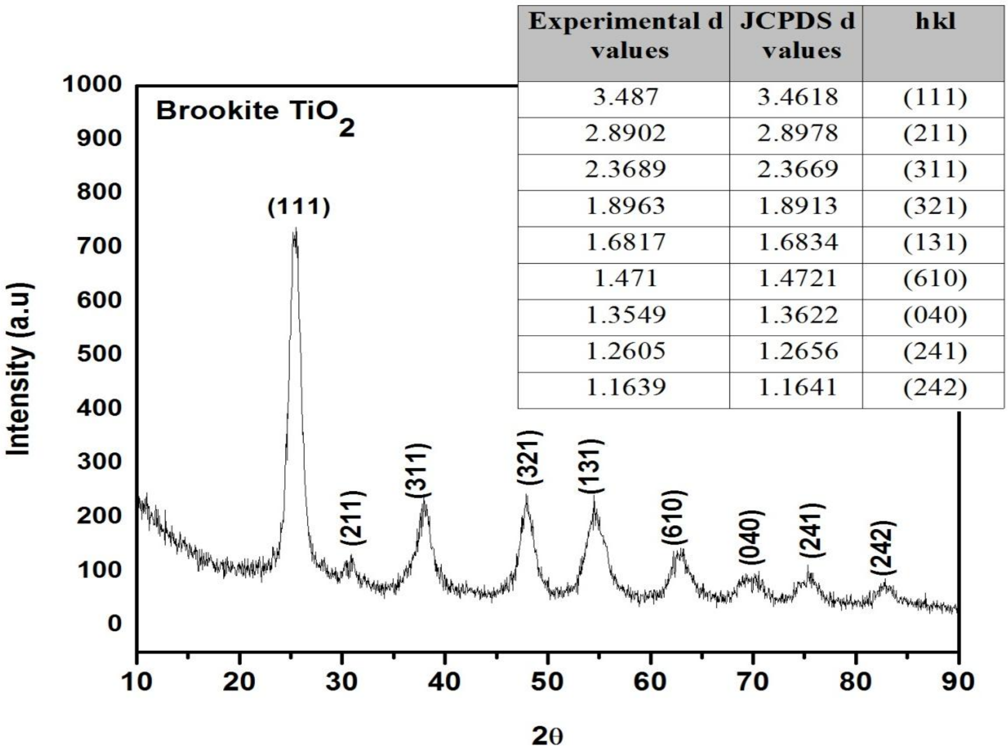
Experimental d values	JCPDS d values	hkl
3.50723	3.52	(101)
2.36296	2.378	(103)
1.89079	1.892	(200)
1.69755	1.6999	(105)
1.66705	1.665	(211)
1.36092	1.3641	(116)
1.33892	1.3378	(220)
1.25985	1.2509	(301)
1.16512	1.1664	(224)

Figure 1: XRD pattern of Anatase TiO_2 *(Sample 1)*



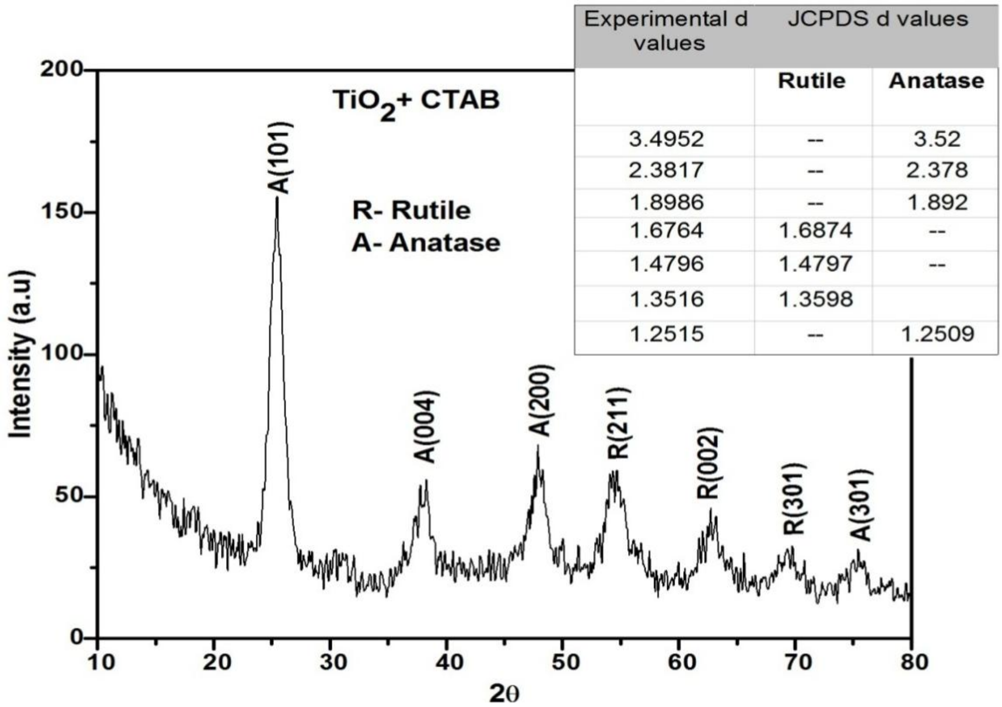
Experimental d values	JCPDS d values	hkl
3.2241	3.247	(110)
2.4832	2.487	(101)
2.1849	2.188	(111)
1.686	1.687	(211)
1.4711	1.479	(002)

Figure 2: XRD pattern of RutileTiO_2



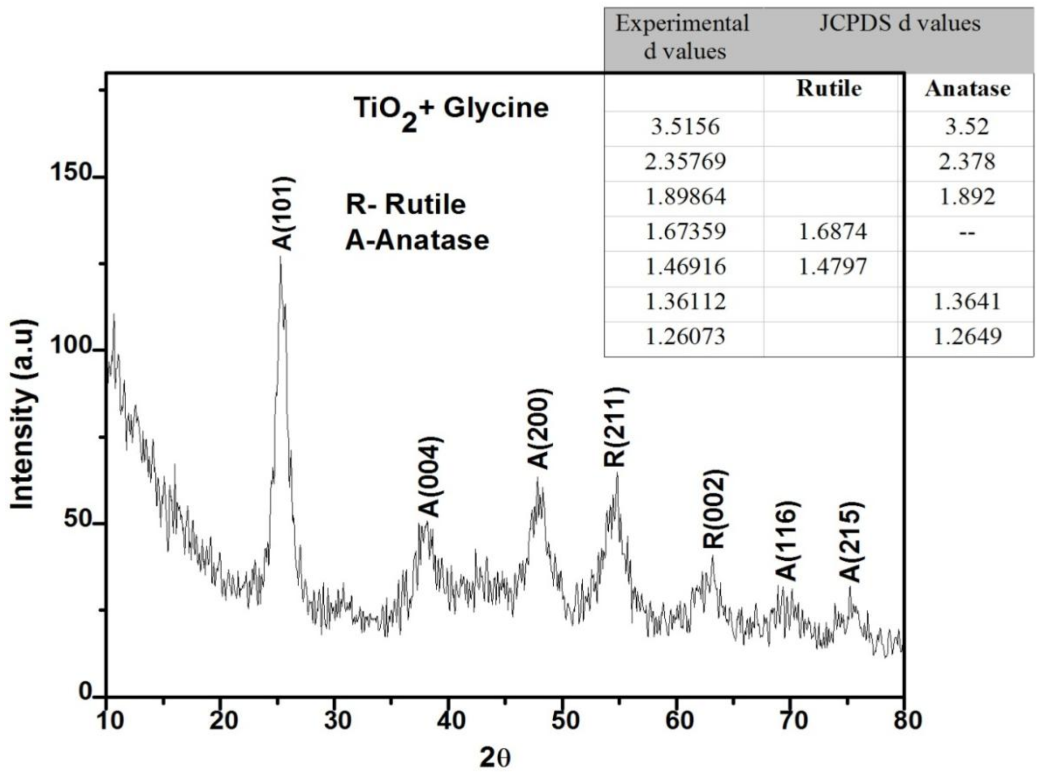
Experimental d values	JCPDS d values	hkl
3.487	3.4618	(111)
2.8902	2.8978	(211)
2.3689	2.3669	(311)
1.8963	1.8913	(321)
1.6817	1.6834	(131)
1.471	1.4721	(610)
1.3549	1.3622	(040)
1.2605	1.2656	(241)
1.1639	1.1641	(242)

Figure 3: XRD pattern of Brookite TiO_2



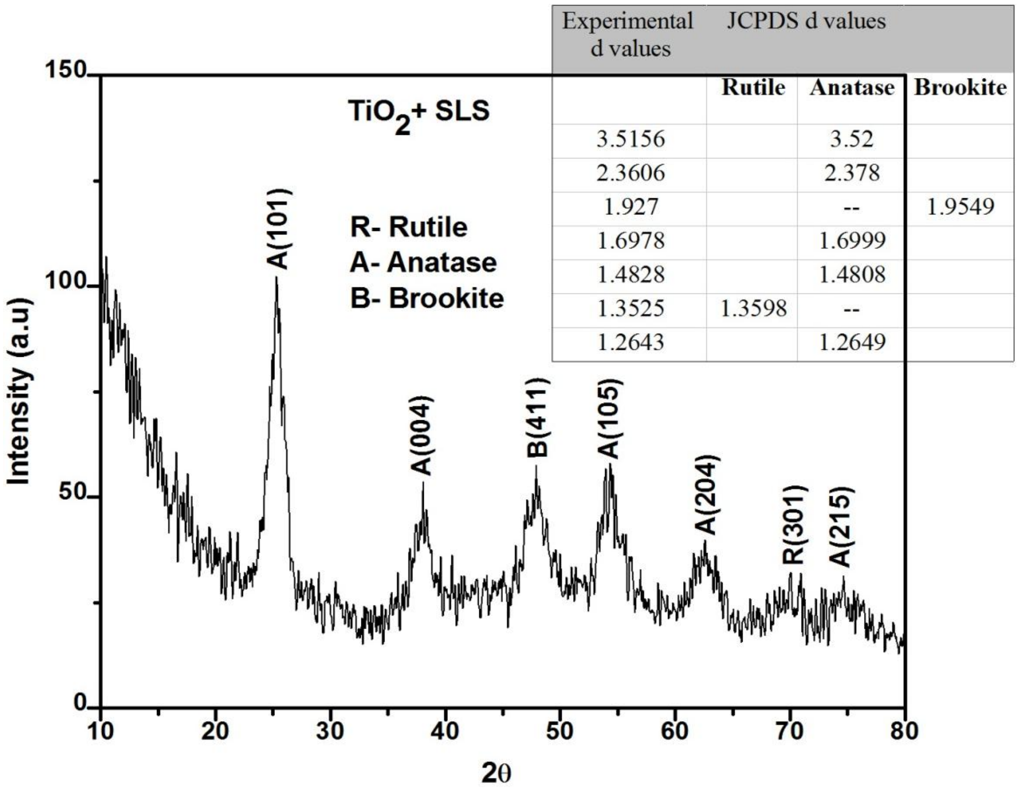
Experimental d values	JCPDS d values	
	Rutile	Anatase
3.4952	--	3.52
2.3817	--	2.378
1.8986	--	1.892
1.6764	1.6874	--
1.4796	1.4797	--
1.3516	1.3598	
1.2515	--	1.2509

Figure 4: XRD pattern of TiO_2 with CTAB



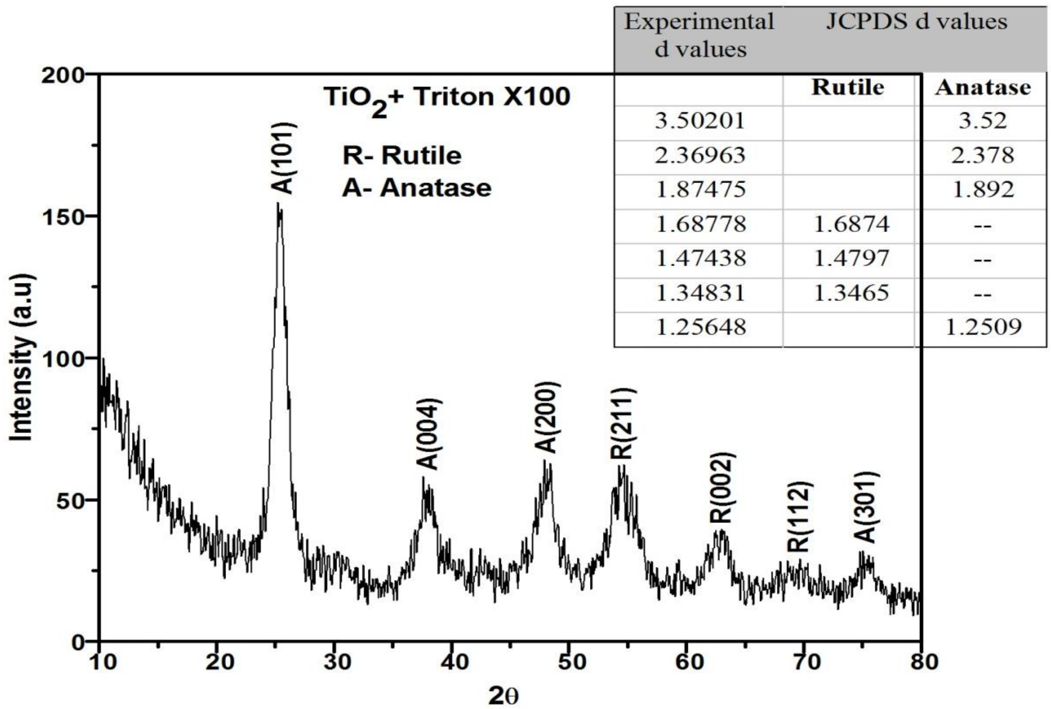
Experimental d values	JCPDS d values	
	Rutile	Anatase
3.5156		3.52
2.35769		2.378
1.89864		1.892
1.67359	1.6874	--
1.46916	1.4797	
1.36112		1.3641
1.26073		1.2649

Figure 5: XRD pattern of TiO_2 with glycine



Experimental d values	JCPDS d values		
	Rutile	Anatase	Brookite
3.5156		3.52	
2.3606		2.378	
1.927		--	1.9549
1.6978		1.6999	
1.4828		1.4808	
1.3525	1.3598	--	
1.2643		1.2649	

Figure 6: XRD pattern of TiO_2 with SLS



Experimental d values	JCPDS d values	
	Rutile	Anatase
3.50201		3.52
2.36963		2.378
1.87475		1.892
1.68778	1.6874	--
1.47438	1.4797	--
1.34831	1.3465	--
1.25648		1.2509

Figure 7: XRD pattern of TiO_2 with Triton X100

Figure 1 shows XRD pattern of sample 1 prepared by hydrothermal method for 24 h. The peaks are sharp and broad. The d values of the peaks match very closely with those reported in JCPDS file (21-1272). The peaks match with the characteristic peaks of Anatase phase of TiO_2. The most intense peak at 2θ value of 25.36° is the characteristic peak of (101) plane.

Figure 2 shows XRD pattern of sample 2 prepared by precipitation method. Peaks with low intensity have been observed. All these peaks are assigned to the Rutile phase of TiO_2 (JCPDS 21-1276). The most intense peak at 2θ value of 27.67° corresponds to the characteristic peak from the plane (110).

Figure 3 shows XRD pattern of sample 3 prepared by hydrothermal method for 2 h. Broad peaks with good intensity have been observed. The peaks correspond to Brookite phase of TiO_2 (JCPDS 76-1934). The most intense peak at 2θ of 25.51° corresponds to (111) plane.

It is worth mentioning that no other peaks of impurity could be detected in all XRD patterns. It confirms the formation of material in pure form. The peaks are broad, which might be due to the formation of material in nano size.

The average crystallite size of the samples is calculated by Scherrer formula. The average crystallite size and lattice strain produced in material is given in Table 1. The average crystallite size is found in a nano size which is evident from the broadening of XRD. The average crystallite size for Anatase, Rutile and Brookite TiO_2 is 14.71 nm, 12.88nm and 5.27 nm respectively. The value of lattice strain is 0.024, 0.002 and 0.071 for Anatase, Rutile and Brookite TiO_2 respectively. A small amount of strain is produced in Rutile TiO_2 which shows the formation of perfect crystal structure of Rutile TiO_2.

The X-ray diffraction patterns of TiO_2 prepared using different surfactants are shown in figure 4 to 7. The comparison of experimentally observed d values with the JCPDS data including their 'hkl' values is given in the tables along with the patterns. The average crystallite size, lattice strain and Anatase content of all the samples are shown in Table 2.

The experimentally observed d values were in good agreement with JCPDS d values. By comparing JCPDS data it is clear that two phases Anatase and Rutile of TiO_2 are present in all the samples. However, the Anatase phase is predominant with preferential orientation of (101) and (004) peaks in all the samples. For the sample 4 prepared using SLS as a surfactant most of the peaks belong to the Anatase and Rutile phase, except for the small peak at 47.10° which corresponds to Brookite phase. No characteristic peaks of other impurities were observed, which indicates that the product has high purity.

A peak broadening has been observed in all the samples which indicate formation of material in smaller size. The average crystallite size of all the samples lies between 4.06 nm and 6.13 nm. The surfactants have lowered the crystallite size. The smaller size indicates that these surfactants can effectively inhibit the grain growth. The phase content of the samples shows that Anatase to Rutile transformation has been inhibited or suppressed by the surfactants and Anatase phase has been stabilized. TiO_2 with SLS shows highest Anatase content. The Anatase content is more than 60% in all the samples. Based on XRD data the lattice strain of TiO_2 samples have been determined. The values of lattice strain are too low for all the samples which confirm the formation material with nearly perfect crystal structure. Lattice strain produced at grain boundaries because of defects.

Table 1: Different structural parameters of prepared samples

Sample	Crystallite size (nm)	Lattice Strain
Anatase TiO_2	14.71	0.024
RutileTiO_2	12.88	0.002
BrookiteTiO_2	5.27	0.071

Table 2: Different structural parameters of prepared samples

Sample	Crystallite size (nm)	Lattice strain (%)	Anatase content (%)
TiO_2 + CTAB	6.13	0.062	66.22
TiO_2 + Glycine	4.06	0.096	60.27
TiO_2 + SLS	4.53	0.083	72.93
TiO_2 + Triton X 100	4.52	0.084	66.83

4.3.2 UV-Visible Characteristics

The UV-Visible absorption spectra of the samples were recorded on a Thermo Fisher Scientific make Evolution 600 Spectrophotometer. The light source is a combination of Tungsten halogen and Deuterium lamps.

The samples were dispersed in ethanol. The dispersion was sonicated for 30 minutes and then transferred to a quartz cuvette for the measurements. The wavelength range was fixed between 200 nm and 900 nm.

The absorption spectra and Tauc's plots of Anatase, Rutile and Brookite TiO_2 are shown in figures 8 to 10 and their structural parameters are given in Table 3. By looking at the absorption spectra of all the samples, it is very clear that absorption edge varies with phase of TiO_2. The highest absorption wavelength is observed for Rutile TiO_2 and lowest for Anatase TiO_2. The value of optical bandgap of Rutile TiO_2 and Brookite TiO_2 has been found to be less in comparison to its reported value [8]. This might be due to the inter band transition rather than bandgap transition [9]. This might be due to the quantum confinement effect as the samples have crystallite size in nanometer. The Anatase TiO_2 shows highest absorption co-efficient while Brookite TiO_2 shows the lowest absorption co-efficient. This shows that photon absorption would be more in Anatase TiO_2. This ascertains the fact that the best phase of TiO_2 to be used for DSSC is the Anatase phase. The calculated values of refractive index for Rutile, Anatase and Brookite are less in comparison to their bulk values of 2.61, 2.49 and 2.58 respectively. This decrease might be due to the change in density of the samples compared to the reported values.

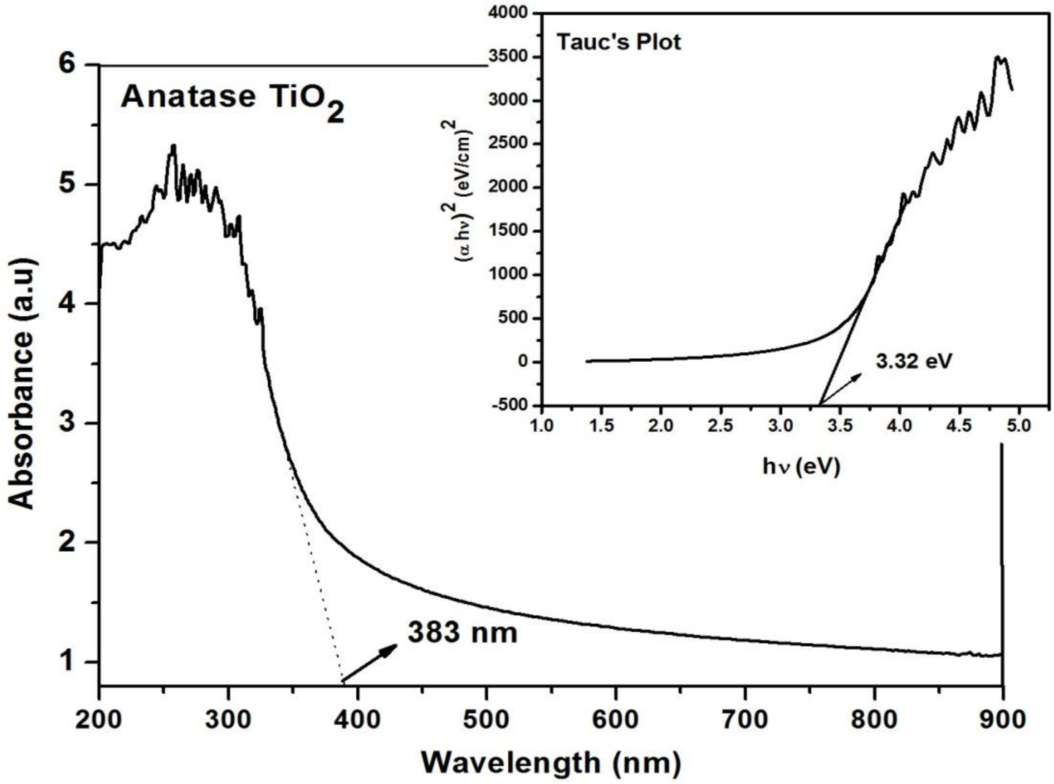


Figure 8: Absorption spectrum and Tauc’s plot for Anatase TiO_2

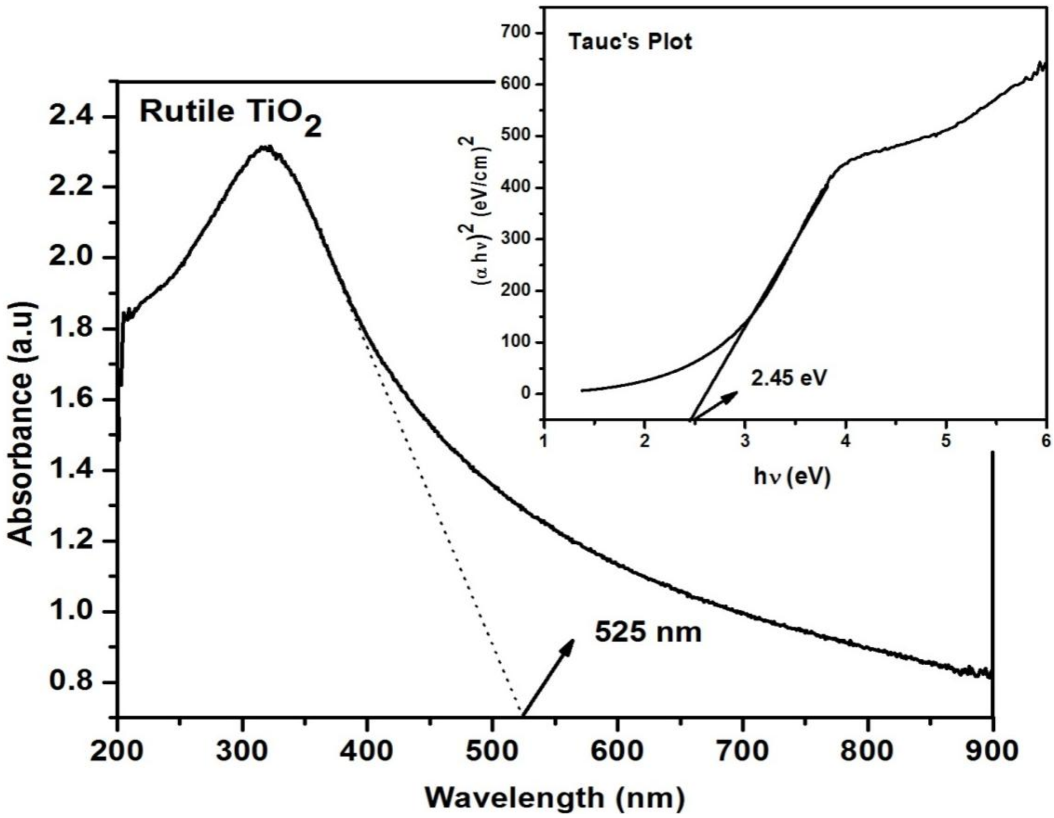


Figure 9: Absorption spectrum and Tauc’s plot for Rutile TiO_2

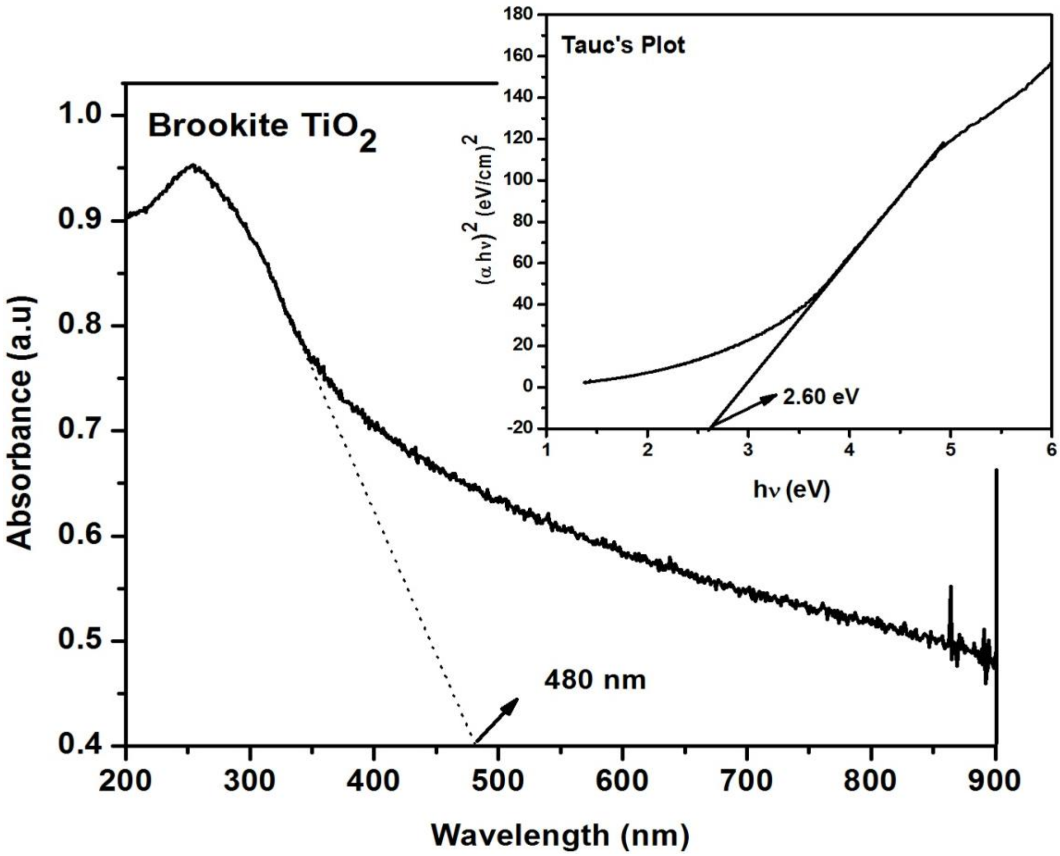


Figure 10: Absorption spectrum and Tauc's plot for Brookite TiO_2

Table 3: Different optical parameters of TiO_2

Sample	Peak Absorption	Optical Bandgap E_g (eV)	Refractive Index η
Anatase TiO_2	270 nm	3.32	2.29
Rutile TiO_2	330 nm	2.45	2.52
Brookite TiO_2	260 nm	2.60	2.47

The optical absorption spectra and related Tauc's plots of TiO_2 prepared using different surfactants are shown in figures 11 to 14. The optical bandgap, absorption co -efficient, extinction co-efficient, refractive index and optical conductivity of all the samples are given in Table 4. The values of all the optical parameters vary with the surfactant used in preparation of TiO_2. The use of surfactants has shifted the absorption edge towards longer wavelength region. The optical bandgap varies between 2.84 eV and 3.07 eV. Surfactants have lowered the refractive index of TiO_2 nanoparticles compare to its reported value **[10]**. The refractive index of all the prepared samples lies in a narrow range between 2.34 and 2.41. TiO_2 sample prepared using Triton X100 shows highest absorption coefficient. Thus TiO_2 prepared with Triton X100 is best among all the samples for its application in dye sensitized solar cell. The sample has mixed phase with a predominance of Anatase.

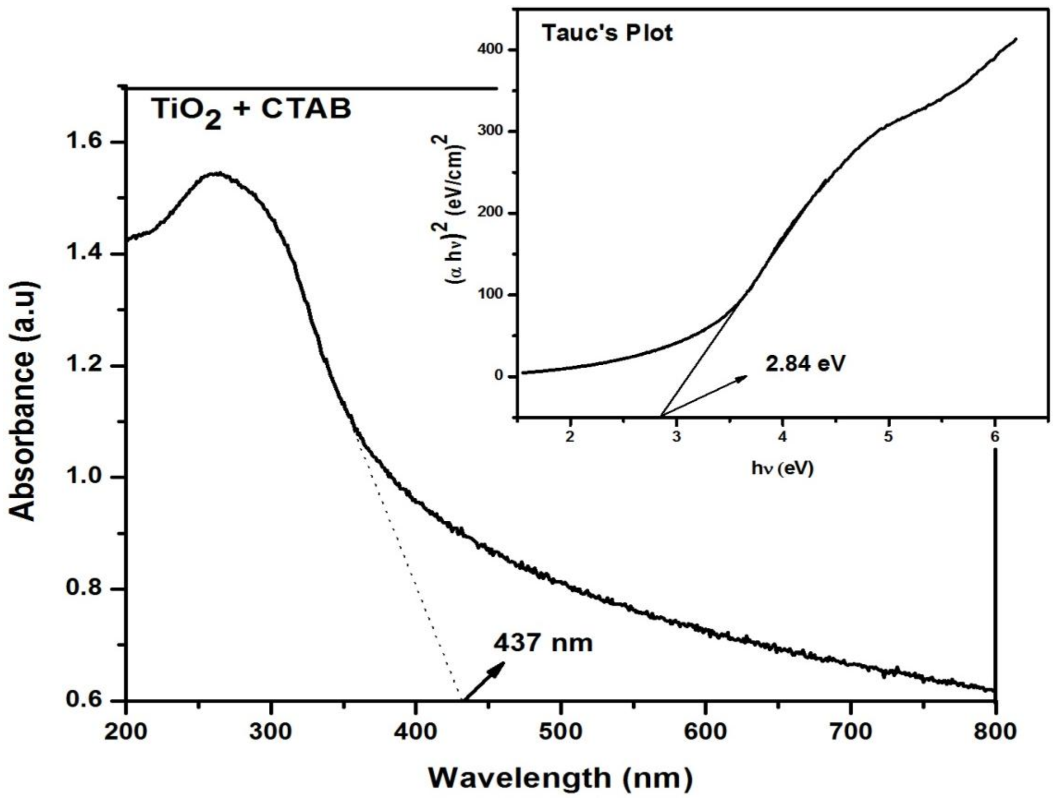


Figure 11: Absorption spectrum and Tauc's plot for TiO_2 with CTAB

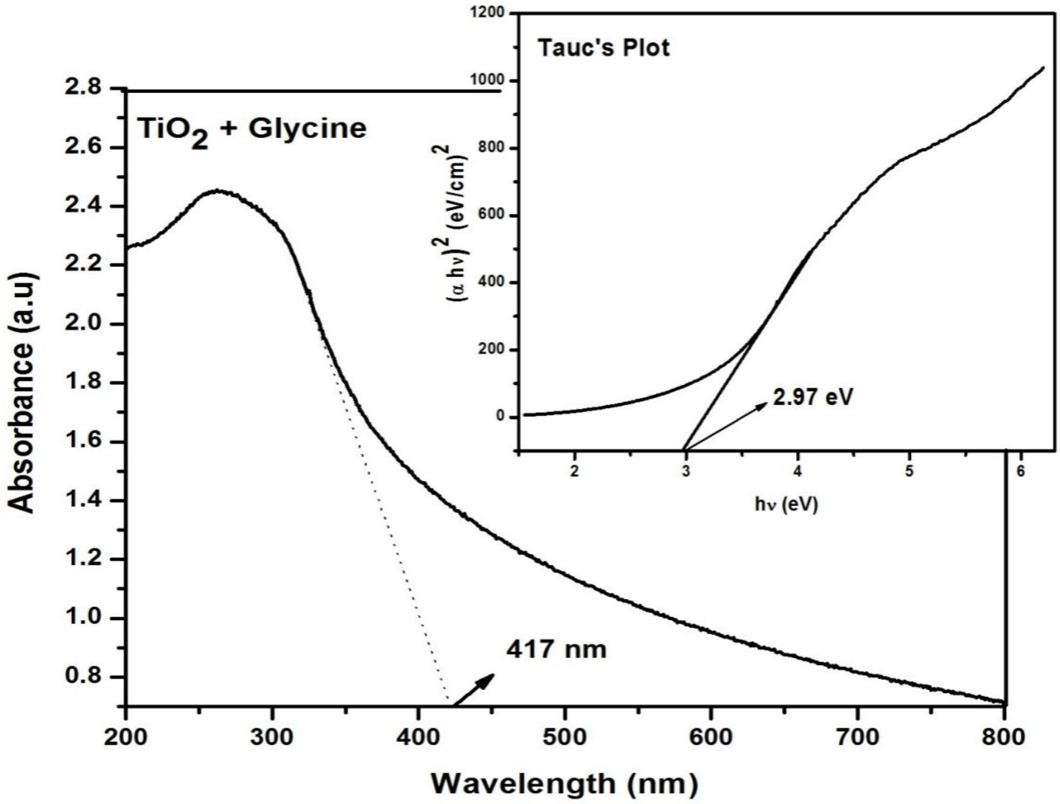


Figure 12: Absorption spectrum and Tauc's plot for TiO_2 with Glycine

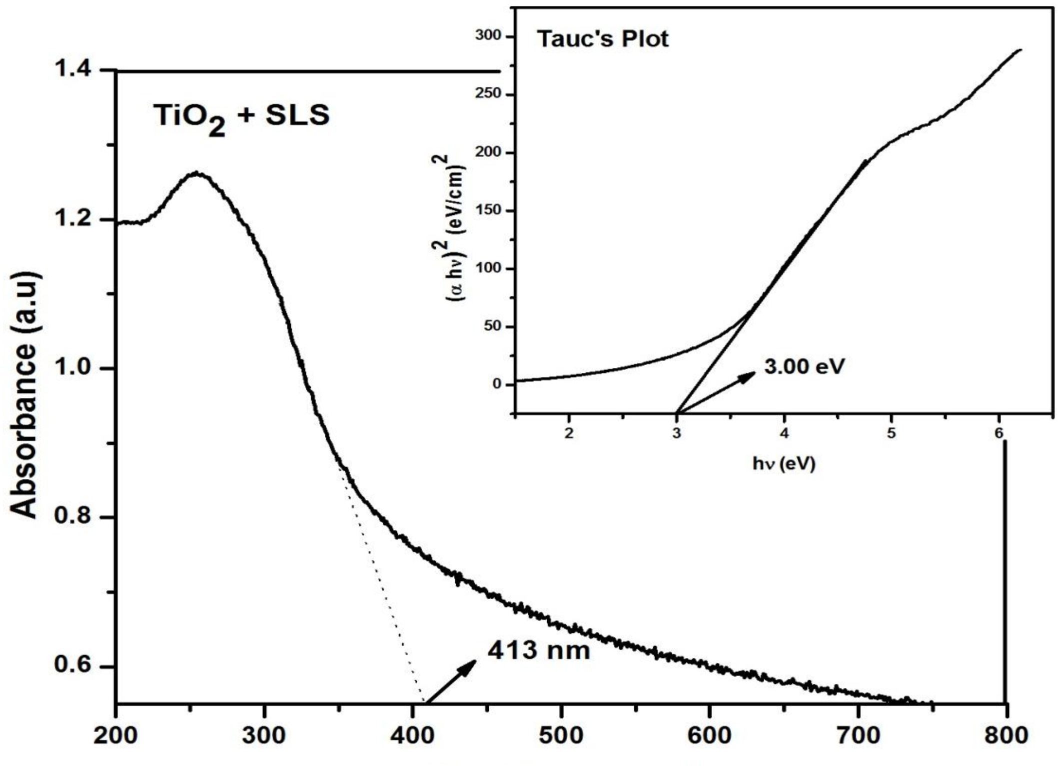


Figure 13: Absorption spectrum and Tauc's plot for TiO_2 with SLS

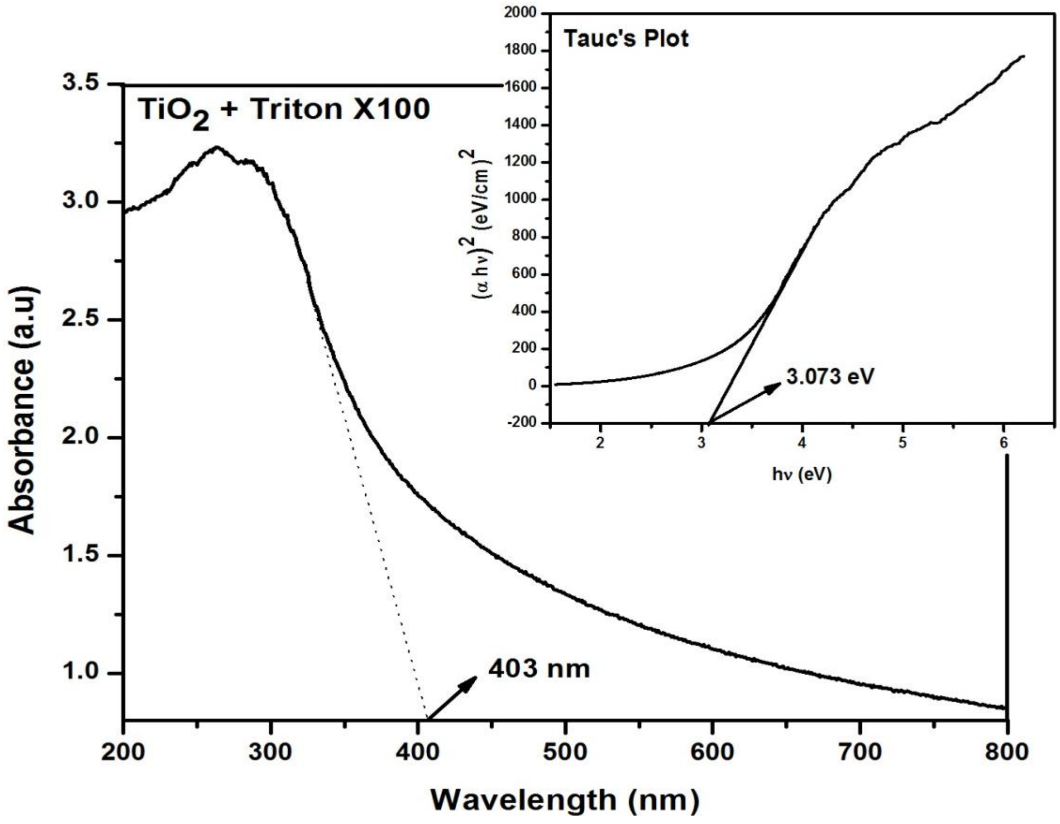


Figure 14: Absorption spectrum and Tauc's plot for TiO_2 with Triton X100

Table 4: Different optical parameters of TiO_2 nanoparticles prepared using surfactants

Sample	Peak Absorption	Optical Bandgap E_g (eV)	Refractive Index η
TiO_2 + CTAB	254 nm	2.84	2.41
TiO_2 + Glycine	260 nm	2.97	2.37
TiO_2 + SLS	255 nm	3.00	2.36
TiO_2 + Triton X100	265 nm	3.07	2.34

4.4 Conclusion

Pure crystallographic phases Rutile, Anatase and Brookite of TiO_2 nanoparticles have been prepared successfully by different methods discussed above. The XRD results confirm the formation of TiO_2 in pure single phase. The crystallite size was found to be 12.88 nm, 14.71 nm and 5.27 nm for Rutile, Anatase and Brookite respectively. The optical bandgap decreases for Rutile and Brookite phases but slightly increases for Anatase TiO_2.

TiO_2 has been prepared using different surfactants by hydrothermal method. The XRD results confirm the formation of TiO_2 nanocrystallites. The average crystallite size of all the samples lies between 4.06 nm and 6.13 nm. Dual phases Rutile and Anatase of TiO_2 are present in all the samples. The Anatase phase is dominant in all samples prepared using surfactants. All the samples contain more than 60% of Anatase phase. A clear shift absorption edge towards longer wavelength for samples prepared with different surfactants has been observed from the UV-visible absorption spectra. The refractive index of TiO_2 has been lowered by surfactants compare to its reported value. A significant impact of surfactants on optical properties of TiO_2 has been observed.

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