INDIAN ACADEMY OF SCIENCES

SUMMER RESEARCH FELLOWSHIP PROGRAMME 2016
FINAL REPORT

SYNTHESIS OF DIFFERENT SIZE TiO_2 NANOPARTICLES AND FABRICATION OF DSSCs

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ACKNOWLEDGEMENTS

I would like to extend my heartiest gratitude to respected Dr. Sameer Sapra, Associate Professor, Dept. of Chemistry, IIT Delhi for his wonderful guidance, soulful encouragement, and constant support at each and every step of the project. It was his rationalist approach from the initial to the final that helped me to develop a better understanding of the subject. It was a ‘once in a lifetime ‘experience to spend my summer under a truly devoted scholastic at one of the best institutes of India.

Also I am indebted to all the friends and colleagues whom I have interacted in the time being of two months. I would immensely like to appreciate the support and guidance of Md. Samim Hassan, Sushma Yadav, Dr. Atanu Jana and Mona Mittal for their generous and helping attitude throughout the entire duration of the work. Also I would like to thank my parents without whose support this project would not have been possible.

The fact that this small journey is nearing its end is sad for me as I would have liked to gain more experience and knowledge from the above mentioned people. It would be grateful of me to lend my hand in nearby future for any other task.

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ABSTRACT

TiO_2 nanoparticles are highly porous[1] and offer a large surface area, and acts as sunlight trapper, but it is not sensitive to visible light. Thus it is sensitized with dye or quantum dots (QD) and used in Dye Sensitized Solar Cells (DSSCs) and Quantum Dot Sensitized Solar Cells (QDSSCs), which are eco-friendly and less expensive[2]as compared to their first and second generation counterparts. The anatase phase of the titanium dioxide is highly desirable for solar cell application due to its low surface energy[3] which is the most important thing at micro level.Hydrothermal method[4]is used for synthesizing TiO_2 nanoparticles which allows variation in particle size with temperature and time variation of the reaction. Using this method of preparation, particles of size 15-20 nm are easily formed, but solar cell efficiencies have been low when these particles were coated with QDs and especially nanoplatelets (NPLs), where the reason is attributed to the ineffective embedding of the QDs (average size 6 nm), NPLs(average size 20 nm) with the TiO_2 nanoparticles. Thus there has been an urgent need of increasing the size of those nanoparticles, with challenges such as maintaining the anatase phase which has a crossover size around 30 nm[1]where it favours the rutile more than anatase.Changes such as increasing concentration, increasing pH of the reaction mixture and increasing reaction time were deployed both separately and collectively to observe their size effects.Both increase in concentration and pH when deployed separately gave particles with more size as depicted by the red shift[5] in their wavelength, and confirmed for one moiety by Transition Electron Microscopy (TEM). Increasing reaction time was not so effective. The actual particle size for the nanoparticles are yet to be confirmed by TEM.

INTRODUCTION

Titanium dioxide or Titanium(IV) dioxide is the naturally occurring oxide of titanium. Its chemical formula is TiO_2. Titanium dioxide occurs naturally in the form of minerals like rutile, anatase and brookite where the crystal structure of the first two are tetragonal and that of the last one is orthorhombic[6].

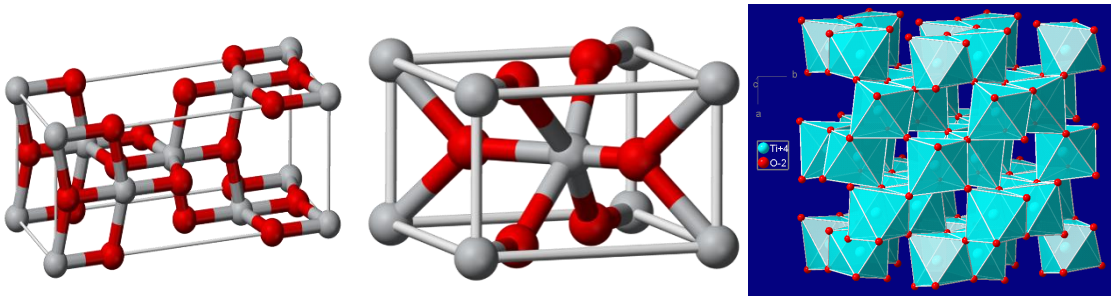

Fig 1: Anatase, rutile and brookite forms of titanium dioxide nanoparticles.

The TiO_2 nanoparticles can be prepared by **hydrothermal** synthesis as well as sol-gel method. The hydrothermal method is preferred in our system due to the fact that the average nanoparticle size can be controlled by varying the processing temperature and time in case of the hydrothermal method while in the case of sol-gel method, it's not possible.

TiO_2 is mostly used as white pigmentdue to its high diffraction index and strong light scattering and incident-light reflection capability. It is these properties and a high UV resistance that make TiO_2 the standard pigment found in white dispersion paints with high hiding power. Since light scattering does not occur anymore innanoscale particles, the white titanium dioxide pigments used are almost exclusively rutile modification particles with grain sizes in the micrometer range. Unlike TiO_2 pigments, nanoscale titanium dioxides are not used as food additives. Currently, they are mainly found in high-factor sun protection creams, textile fibers or wood preservatives. Due to the hydrophilic character of titanium dioxide, water forms a closed film on the surface in which pollutants and degradation products can be easily carried away[7]. House paints or tiles containing TiO_2 particles thus are self-cleaning and pollutant-degrading.The **photocatalytic**[8] activity, which is another property of TiO_2, is increased considerably through the high surface-to-volume ratio of the nanoparticles as compared to that of macroparticles. The titanium dioxide nanoparticles are used in **DSSCs** and **QDSSCs**.

The Shockley-Queisser thermodynamics puts a limit of efficiency (~33%) upon the first and the second generation solar cells calling it the time for the third generation solar cells that include DSSCs and QDSSCs. The physical and chemical properties of QDs are size dependent[9]. They have high tunability of band gap, narrow emission spectrum, good photostability, broad emission spectra, high extinction coefficient, multiple exciton generation.

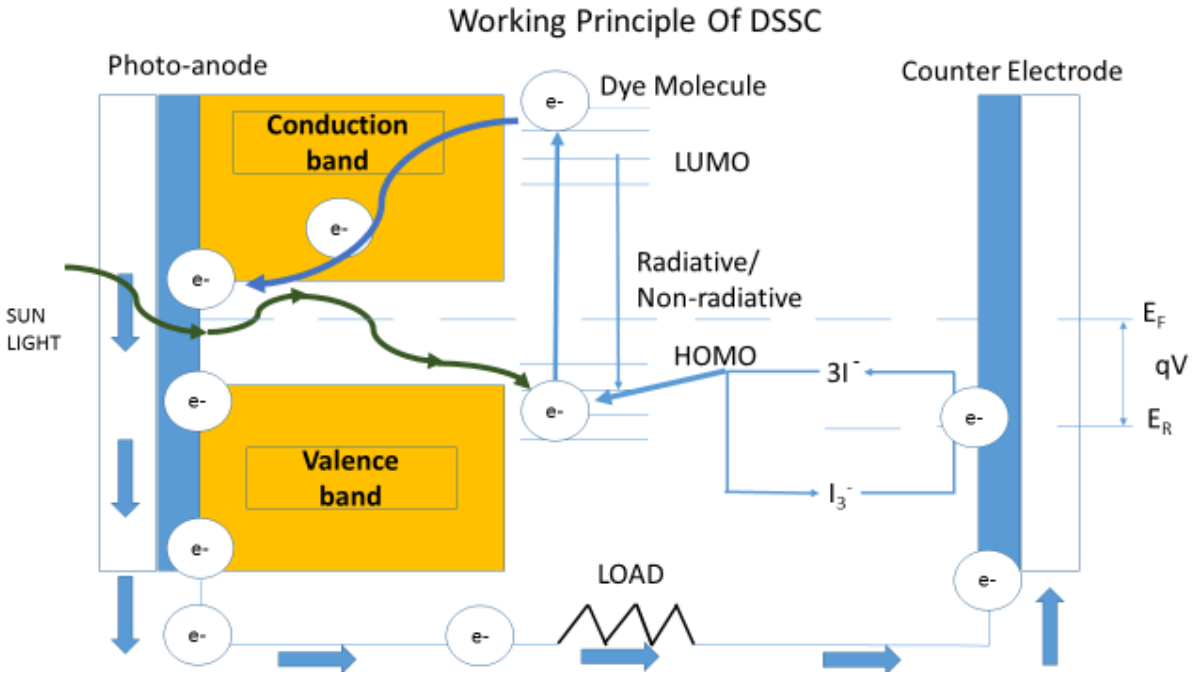

Fig 2: Schematic illustration of the electron flow in an operating DSC. Dye excitation, electron injection from photoexcited dye into TiO2, charge collection at working electrode, reduction of triiodide at counter electrode and regeneration (reduction) of the oxidized dye.

DSSCs and QDSSCs are made of two electrodes, the anode and the cathode. These electrodes are made from a specific glass that has a Transparent Conductive Oxide (TCO) coating on one side. The TCO material is a thin layer of fluorine-doped tin oxide, also called FTO. The transparency of the substrate allows sunlight to enter the cell while its conductive surface collects charges. TiO_2 nanoparticles are coated on the FTO glass which have porous network and it offers an inner surface that is a thousand times greater than the equivalent flat area, and acts like a "light sponge" in which sunlight can get trapped. Titaniumdioxide is a white semiconductor that is not sensitive to visible light. Therefore, the titania particles are sensitized with a layer of dye molecules or QD absorbing light in the visible spectrum. A sensitizer anchored to the surface of a TiO_2 semiconductor absorbs the light, and charge

separation occurs at the interface by photo-induced electron injection from the dye into the conduction band of $TiO_2$and the hole remains in the dye molecule or QD. Injected electrons migrate through the titanium dioxide particles and reach the TCO glass of the anode, the negative terminal of the solar cell. And because of the redox couple present in the electrolyte, electrons can finally be transported from the cathode's surface to the oxidized dye molecules or QD.

The important components of DSSCs and QDSSCs are:-

• **Working electrode (WE):** porous nanostructured TiO_2 attached to a conducting substrate, often fluorine-doped tin oxide (FTO).

• **Counter electrode (CE):** platinized conducting substrate.

• **Light-absorbing layer:** adsorbed sensitizing dye or quantum dots.

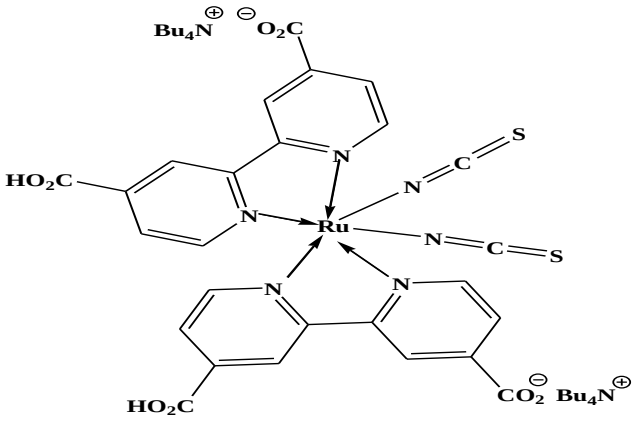

Fig 3: Structure of Ru-N719 red dye; $C_{58}H_{88}N_8O_8RuS_2$; Molecular Weight.: 1188.5 g

• **Redox system (charge conducting medium):** liquid electrolyte containing the redox couple iodide/triiodide (I^-/I_3^-)

The key parameter of I-V curve includes**short circuit current (Isc),open circuit voltage (Voc),Pmax** etc.

Short circuit current, Isc, flows with zero external resistance (V=0) and is the maximum current delivered by the solar cell at any illumination level. Open circuit voltage, Voc, is the potential that develops across the terminals of the solar cell when the external load resistance is very large. Pmax is the maximum power delivered at the infinite current.

Fill Factor (FF) is defined as: $FF = P_{max} / (V_{oc} x\ I_{sc})$

Efficiency: The efficiency of solar cell is the ratio of the electrical power it delivers to the load to the optical power incident of the cell. The overall solar power conversion efficiency can be calculated as

$\eta = P_{max}/(I_s \times A_s)$

where A_s is the working area of the solar cell (m^2) and I_s is the irradiance of the incident light (W/m^2), which is usually taken as 1000 W/m^2(1 Sun). Another important parameter, used to characterize the cells, is the current density per unit area of the cell, denoted by J_{sc}.

$J_{sc} = I_{sc}/Area$

MATERIALS AND INSTRUMENTATION

Materials Required:-

$TiCl_4$ (Spectrochem), liquor ammonia (25%, Fischer Scientific), hydrogen peroxide solution (30% w/v, Fischer Scientific), FTO glasses (2cm x2cm), TiO_2Nano powder (20 nm), hexachloroplatinic acid (Sigma Aldrich), Ru N-719 dye (acid form, Sigma Aldrich), potassium iodide, ethanol (99.99%, ACS, ISO), isopropanol, acetone (99%, EMPLURA), toluene (99.5%, Fisher Scientific), formamide (98%, Fisher Scientific), sodium sulphide (>55-58%, CDH), hexane (Sd fine lim.), tertiary butyl alcohol (98%, Fischer Scientific). All chemicals were used as received.

Instrumentation:-

1. **UV-visible measurements:** Absorption spectra were collected with a Perkin-Elmer Lambda 1050 spectrophotometer using 1 cm quartz cuvette over the range of 200-800 nm.
2. **Photoluminescence studies:** The fluorescence spectra were recorded on Perkin-Elmer LS-55 spectrometer with constant 10 nm excitation and 5 or 2.5 nm emission slit width with an excitation wavelength of 220 nm.
3. **Scanning Electron Microscopy images (SEM):**TEM images were captured using Delong instruments
4. **Transmission Electron Microscopy images (TEM):** TEM images were captured using Delong instruments.
5. **X-ray Diffraction (XRD):** Powder X-ray diffraction (PXRD) patterns were taken on a Bruker D8 Advance Diffractometer with Ni-filtered Cu K_α radiation. Fast scanning was done with 2(theta) values ranging from 10 to 80 degrees.
6. **I-V Characteristics:**Xenon light source with AM1.5G filter and irradiance of 1000W/$m^2$for illumination ofsolar cell was used and Keithly source meter (Model No. 2611A) was used for measurement.

METHODOLOGY

Expt. No.	Amount of $TiCl_4$(ml)	Amount of NH_3(ml)	Amount of NH_3(ml)	pH of solution	Reaction time (hrs)
1	1.8	18	62	7	42
2	3.6	36	82	9	24
3	3.6	36	82	9	48
4	1.8	18	62	9	24
5	3.6	36	124	7	24
6	3.6	36	124	7	48
7	1.8	18	62	7	24

Table 1: Experimental conditions in reactions 1-7

Experiment No. 1

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, and observing the size effect of the increase in reaction time from 24 hours to 42 hours.

Procedure:-

0.33 M (1.8 ml) $TiCl_4$(spectrochem) was dissolved in 50 ml distilled water in cold ice bath in inert atmosphere to prevent precipitation. The needle was immediately washed with ethanol. Stirring was done for 30 minutes.18 ml liquor ammonia solution (Fischer Scientific) was added dropwise for precipitation. After that, the precipitate was filtered using vacuum pump, with 2 litres distilled water passed over the layer of 2 whatmann filter paper over 3-4 hours.

The precipitate was collected in a reagents bottle and placed in an ice bath. The precipitate was treated with 62 ml hydrogen peroxide solution (Fischer Scientific) till the bubbles initially formed started disappearing. After 4-5 hours a clear reddish coloured solution was formed. The solution was placed in an autoclave for 42 hours at 190 degree Celsius. The solution was taken out after 1 day. The solution was centrifuged for 30 minutes at around 5000 rpm. The liquid part was left out and the centrifuge tube was sealed from above by aluminium foil with holes in it and kept inside oven for drying for 1 day. The dried particles are then crushed using mortar and pestle and then made ready for characterization.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy.

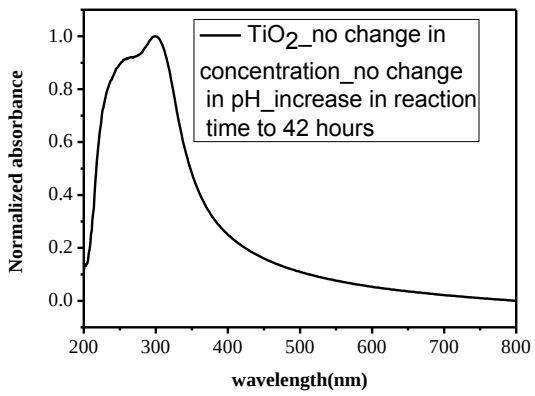

Figure 4: UV-Visible absorbance spectra.

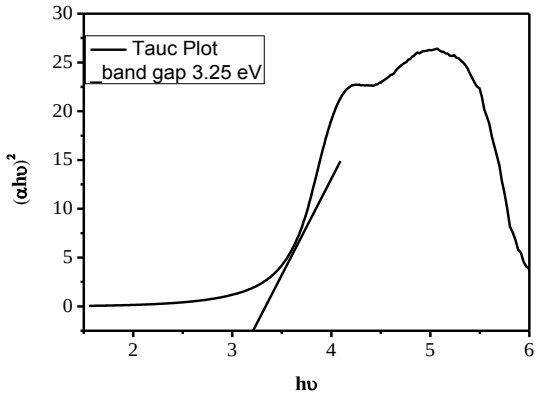

Figure 5: Tauc Plot, band gap 3.25 Ev

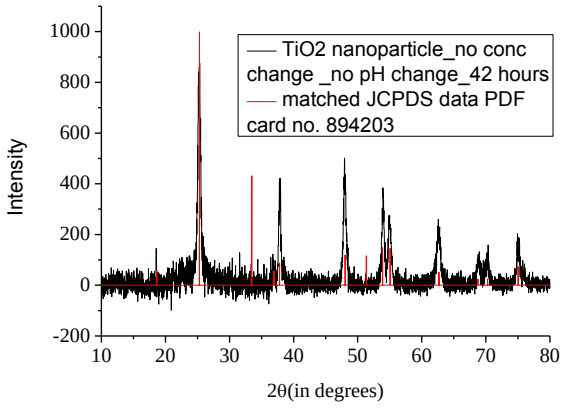

Figure 6: PXRD of TiO2 nanoparticle. Matching with standard JCPDS PDF card (894203) the structure of TiO_2 nanoparticle is anatase phase and tetragonal crystal structure.

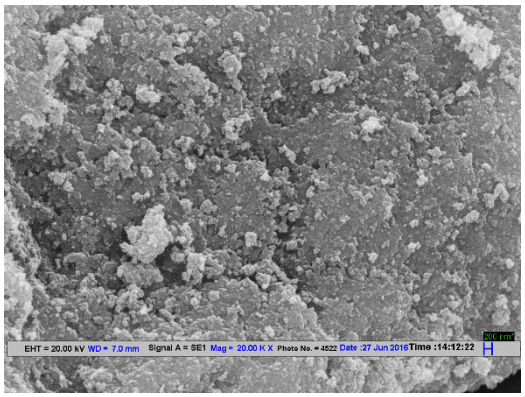

Figure 7(a): SEM image. EHT = 20.00 KV and Mag. = 20.00 KX

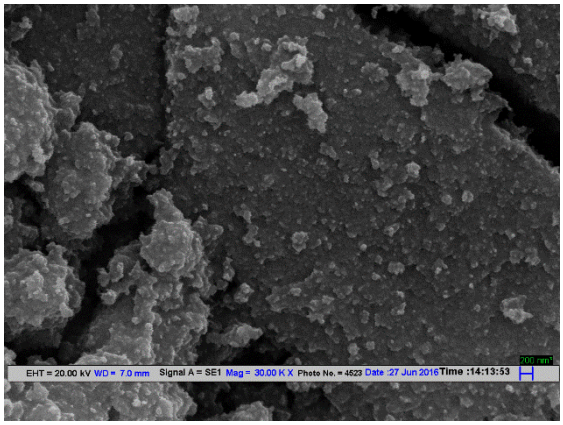

Figure 7(b): SEM image. EHT = 20.00 KV and Mag. = 30.00 KX

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data. UV-VIS spectroscopy was done and maximum wavelength was noted at 300 nm. Tauc plot was done and it gave the band gap to be 3.25 eV. The particle size was calculated using Debye-Scherrer formula for the planes (101), (004) and (200) respectively and it gave size as 15.1 nm, 25.6 nm and 18.0 nm respectively. SEM images were also taken but it could not tell about the particle size. TEM images are yet to be taken and the actual particle size would be confirmed from that.

Experiment No. 2

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, and observing the size effect of the doubling the concentration[10] of the reactants and increasing the pH[11] of the solution from 7 to 9, while keeping the reaction time as 24 hours.

Procedure:-

We followed the same procedure as in the case of the first experiment with some variations. We used 0.66 M (3.6 ml) $TiCl_4$(spectrochem), 36 ml liquor ammonia solution (Fischer Scientific) in our experiment. The precipitate formed after ammonia treatment and filtration was treated with 82 ml hydrogen peroxide solution (Fischer Scientific) till the bubbles initially formed started disappearing. The pH was checked and was noted to be around 7 using a pH paper. A 1 M sodium hydroxide solution was prepared by adding 1 gram of

sodium hydroxide in 25 ml of water. The prepared solution was added to the reddish coloured solution till the pH reached to around 9 that was confirmed by the use of the pH paper.The solution was placed in an autoclave for 24 hours at 190 degree Celsius. After removing it from the autoclave, it was dried in centrifuge tube covered with aluminium foil with holes in it. The dried particles are then crushed using mortar and pestle and then made ready for characterization.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy.

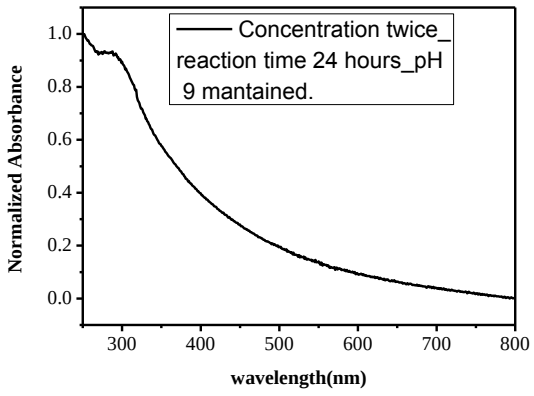

Figure 8: UV-Visible absorbance spectra.

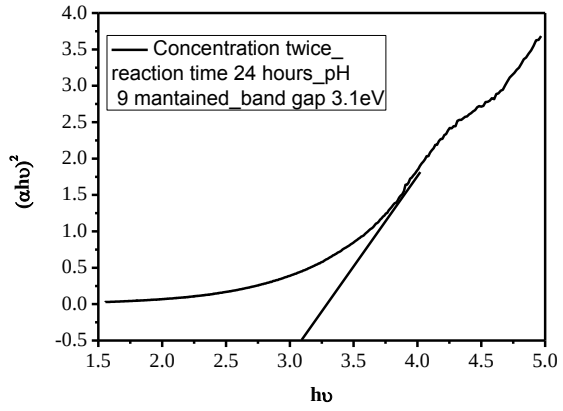

Figure 9: Tauc Plot, band gap 3.1 eV

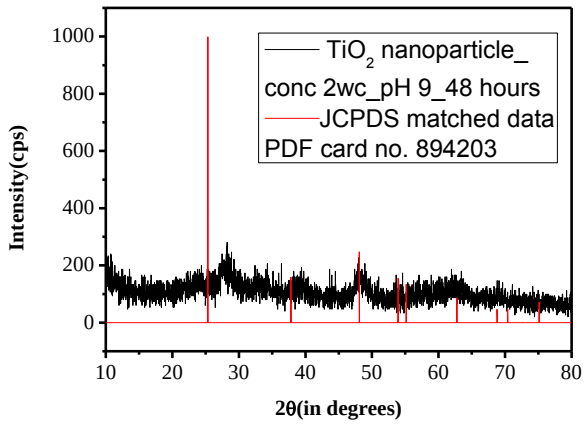

Figure 10(a): PXRD of TiO2 nanoparticle. Matching with standard JCPDS PDF card (894203) the structure of TiO_2 nanoparticle is anatase phase and tetragonal crystal structure.

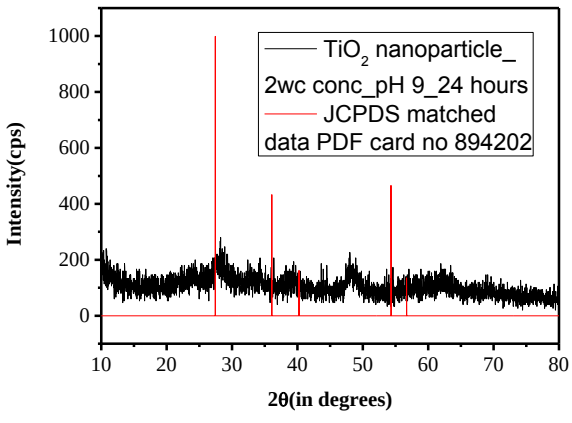

Figure 10(b): PXRD of TiO2 nanoparticle. Matching with standard JCPDS PDF card (894202) the structure of TiO_2 nanoparticle is rutile phase and tetragonal crystal structure.

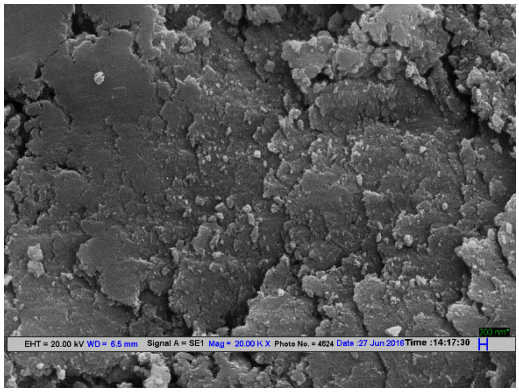	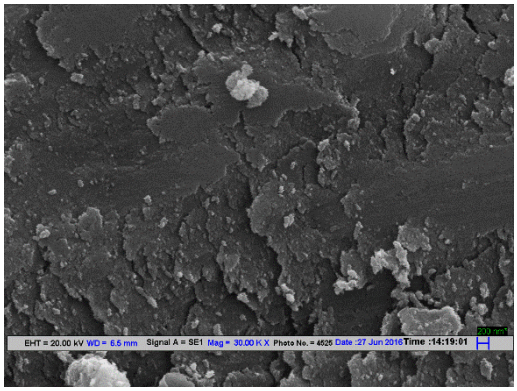
Figure 11(a): SEM image. **EHT = 20.00 KV and Mag. = 20.00 KX**	**Figure 11(b): SEM image.** **EHT = 20.00 KV and Mag. = 30.00 KX**

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data, but it had a mixture of rutile and anatase phase. UV-VIS spectroscopy was done and maximum wavelength was noted at 291 nm. Tauc plot was done and it gave the band gap to be 3.1 eV. The particle size was calculated using Debye-Scherrer formula but the sizes were as low as 4-5 nm. SEM images were also taken but it could not tell about the particle size. TEM images are yet to be taken and the actual particle size would be confirmed from that.

Experiment No. 3

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, and observing the size effect of the doubling the concentration of the reactants, increasing the pH of the solution from 7 to 9, and increasing the reaction time to 48 hours.

Procedure:-

We followed the same procedure as in the case of the first experiment with some variations. We used 0.66 M (3.6 ml) $TiCl_4$(spectrochem), 36 ml liquor ammonia solution (Fischer Scientific) in our experiment. The precipitate formed after ammonia treatment and filtration was treated with 82 ml hydrogen peroxide solution (Fischer Scientific) till the bubbles initially formed started disappearing. The pH was checked and was noted to be around 7 using a pH paper. A 1 M sodium hydroxide solution was prepared by adding 1 gram of sodium hydroxide in 25 ml of water. The prepared solution was added to the reddish coloured

solution till the pH reached to around 9 that was confirmed by the use of the pH paper.The solution was placed in an autoclave for 48 hours at 190 degree Celsius. After removing it from the autoclave, it was dried in centrifuge tube covered with aluminium foil with holes in it. The dried particles are then crushed using mortar and pestle and then made ready for characterization.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy.

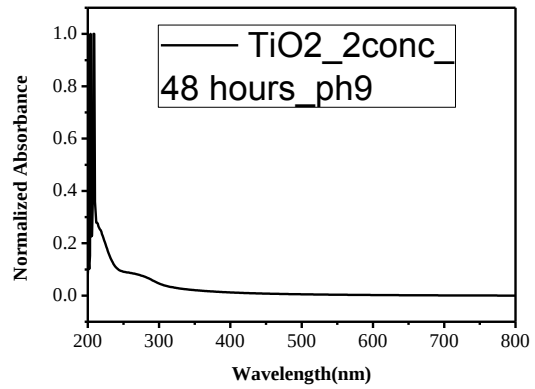

Figure 12: UV-Visible absorbance spectra.

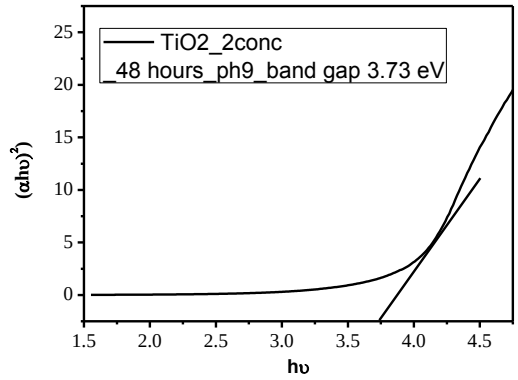

Figure 13: Tauc Plot, band gap 3.73 eV

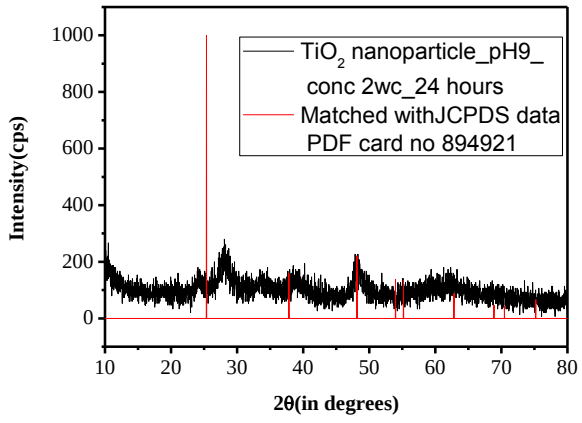

Figure 14(a):Matching with standard JCPDS PDF card (894921) the structure of TiO_2 nanoparticle is anatase phase and tetragonal crystal structure.

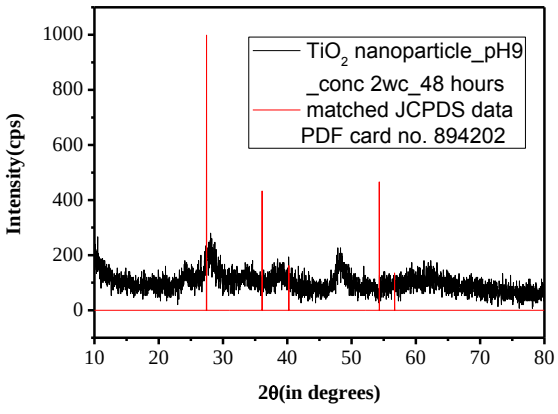

Figure 14(b):PXRD of TiO2 nanoparticle. Matching with standard JCPDS PDF card (894202) the structure of TiO_2 nanoparticle is rutile phase and tetragonal crystal structure.

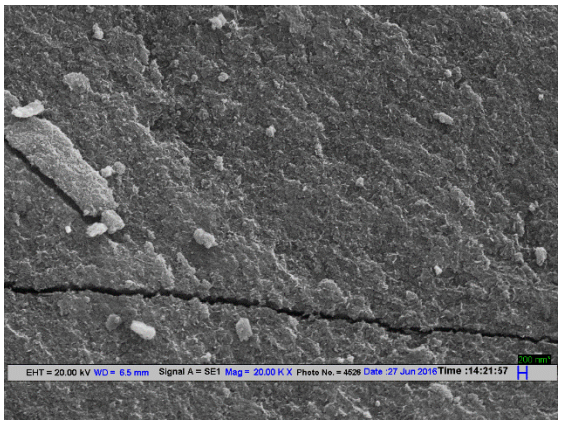	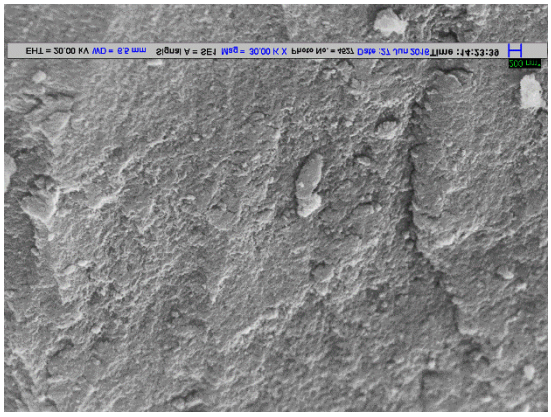
Figure 15(a): SEM image. **EHT = 20.00 KV and Mag. = 20.00 KX**	**Figure 15(b): SEM image.** **EHT = 20.00 KV and Mag. = 30.00 KX**

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data, but it gave a mixture of rutile and anatase phase. UV-VIS spectroscopy was done and maximum wavelength was noted at 272 nm. Tauc plot was done and it gave the band gap to be 3.73 eV. The particle size was calculated using Debye-Scherrer formula but the sizes were as low as 4-5 nm. SEM images were also taken but it could not tell about the particle size. TEM images are yet to be taken and the actual particle size would be confirmed from that.

Experiment No. 4

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, and observing the size effect of increasing the pH of the solution from 7 to 9, while keeping the reaction time as 24 hours and without increasing the concentration of the reactants.

Procedure:-

We followed the same procedure as in the case of the first experiment with some variations. We used 0.33 M (1.8 ml) $TiCl_4$(spectrochem),18 ml liquor ammonia solution (Fischer Scientific) in our experiment. The precipitate formed after ammonia treatment and filtration was treated with 62 ml hydrogen peroxide solution (Fischer Scientific) till the bubbles initially formed started disappearing. The pH was checked and was noted to be around 7 using a pH paper. A 1 M sodium hydroxide solution was prepared by adding 1 gram of

sodium hydroxide in 25 ml of water. The prepared solution was added to the reddish coloured solution till the pH reached to around 9 that was confirmed by the use of the pH paper.The solution was placed in an autoclave for 24 hours at 190 degree Celsius. After removing it from the autoclave, it was dried in centrifuge tube covered with aluminium foil with holes in it. The dried particles are then crushed using mortar and pestle and then made ready for characterization.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy, X-Ray Diffraction, Transition Electron Microscopy.

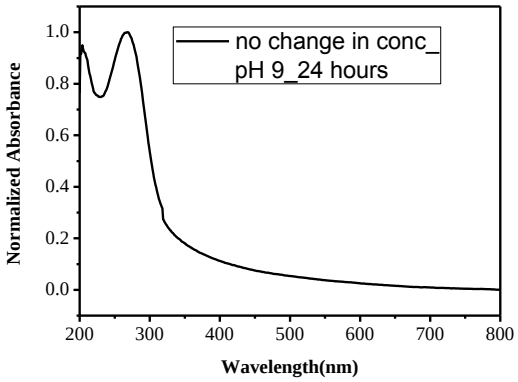

Figure 16: UV-Visible absorbance spectra.

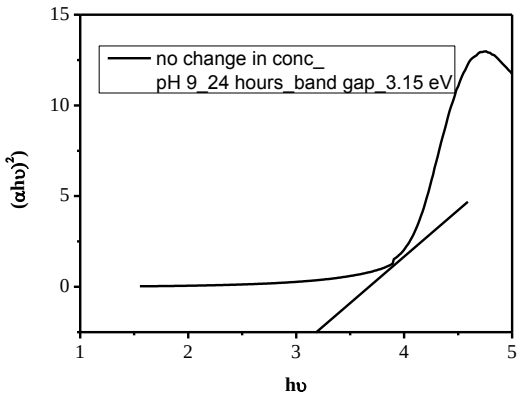

Figure 17: Tauc Plot, band gap 3.15 eV

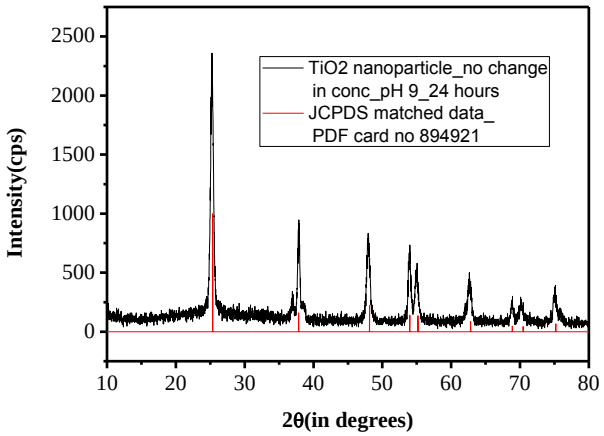

Figure 18: PXRD of TiO2 nanoparticle. Matching with standard JCPDS PDF card (894921) the structure of TiO_2 nanoparticle is anatase phase and tetragonal crystal structure.

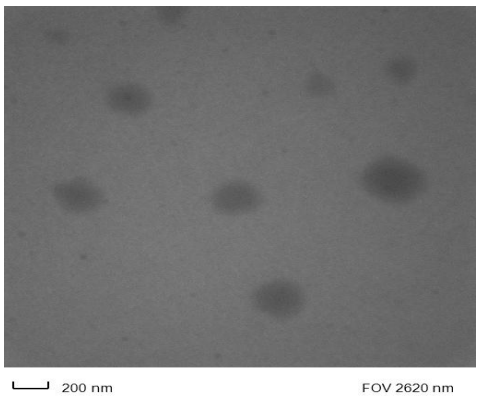

Figure 19: TEM image of TiO_2 nanoparticle. Particle size is around 60 nm.

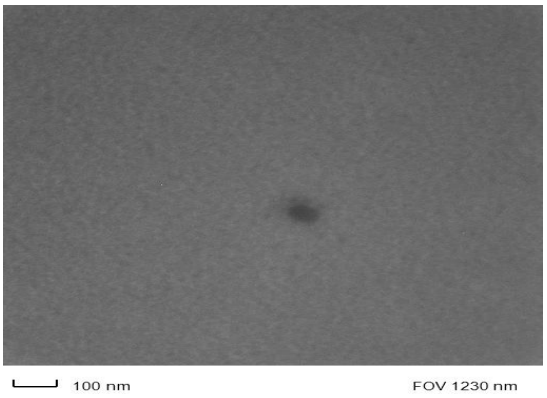

Figure 20: TEM image of TiO_2 nanoparticle. Particle size is around 40 nm.

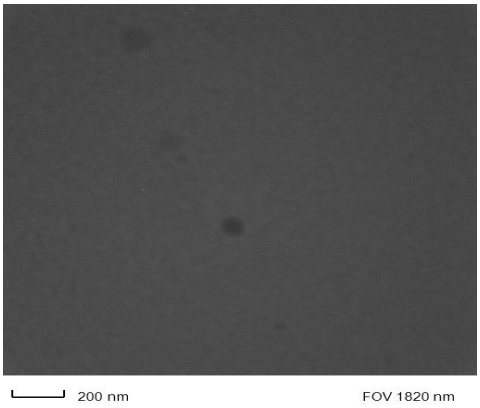

Figure 21: TEM image of TiO_2 nanoparticle. Particle size is around 40 nm.

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data. UV-VIS spectroscopy was done and maximum wavelength was noted at 319.1 nm. Tauc plot was done and it gave the band gap to be 3.15 eV. The particle size was calculated using Debye-Scherrer formula for the planes (101), (004) and (200) respectively and it gave size as 17.5 nm, 30.4 nm and 18.0 nm respectively. TEM images were taken and the particle size was nearly 40 nm.

Experiment No. 5

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, and observing the size effect by doubling the concentration of the reactants, while keeping the reaction time as 24 hours.

Procedure:-

We followed the same procedure as in the case of the first experiment with some variations. We used 0.66 M (3.6 ml) $TiCl_4$(spectrochem), 36 ml liquor ammonia solution (Fischer Scientific) in our experiment. The precipitate formed after ammonia treatment and filtration was treated with 124 ml hydrogen peroxide solution (Fischer Scientific) till the bubbles initially formed started disappearing. The solution was placed in an autoclave for 24 hours at 190 degree Celsius. After removing it from the autoclave, it was dried in centrifuge tube

covered with aluminium foil with holes in it. The dried particles are then crushed using mortar and pestle and then made ready for characterization.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy and X-Ray Diffraction.

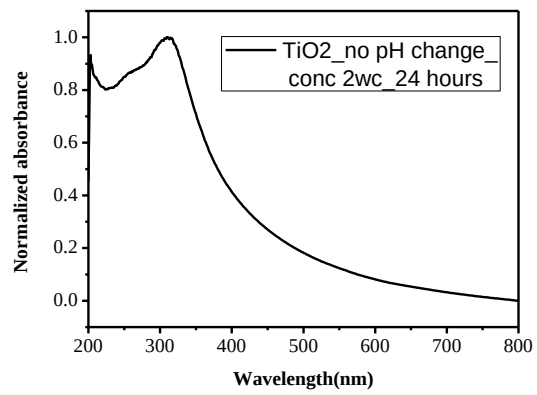

Figure 22: UV-Visible absorbance spectra.

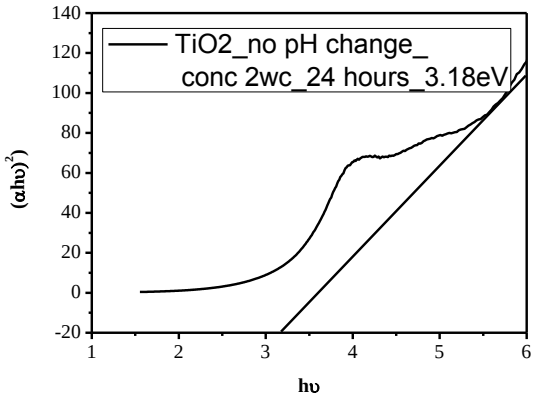

Figure 23: Tauc Plot, band gap 3.18 eV

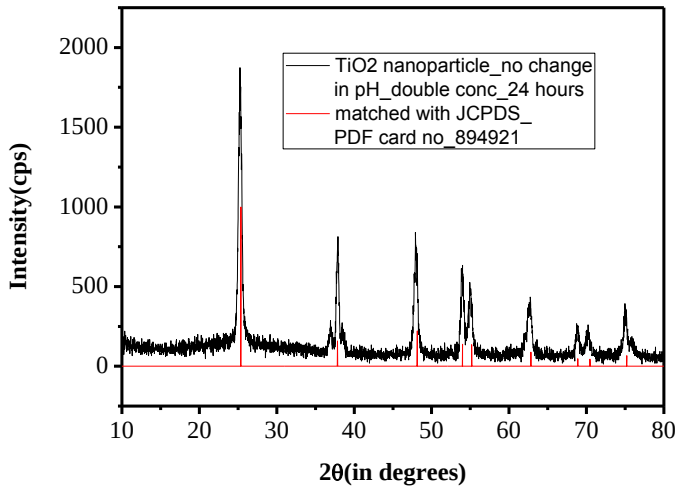

Figure 24: PXRD of TiO2 nanoparticle.
Matching with standard JCPDS PDF card (894921) the structure of TiO_2 nanoparticle is anatase phase and tetragonal crystal structure.

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data. UV-VIS spectroscopy was done and maximum wavelength was noted at 313.4 nm. Tauc plot was done and it gave the band gap to be 3.18 eV. The particle size was calculated using Debye-Scherrer formula for the planes (101), (004) and (200) respectively and it gave size as 17.6 nm, 24.9 nm and 16.8 nm respectively. SEM and TEM images are yet to be taken and the actual particle size would be confirmed from that.

Experiment No. 6

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, and observing the size effect of the doubling the concentration of the reactants, while keeping the reaction time as 48 hours.

Procedure:-

We followed the same procedure as in the case of the first experiment with some variations. We used 0.66 M (3.6 ml) $TiCl_4$(spectrochem), 36 ml liquor ammonia solution (Fischer Scientific) in our experiment. The precipitate formed after ammonia treatment and filtration was treated with 124 ml hydrogen peroxide solution (Fischer Scientific) till the bubbles initially formed started disappearing. The prepared solution was added to the reddish coloured solution till the pH reached to around 9 that was confirmed by the use of the pH paper.The solution was placed in an autoclave for 48 hours at 190 degree Celsius. After removing it from the autoclave, it was dried in centrifuge tube covered with aluminium foil with holes in it. The dried particles are then crushed using mortar and pestle and then made ready for characterization.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy and X-Ray Diffraction.

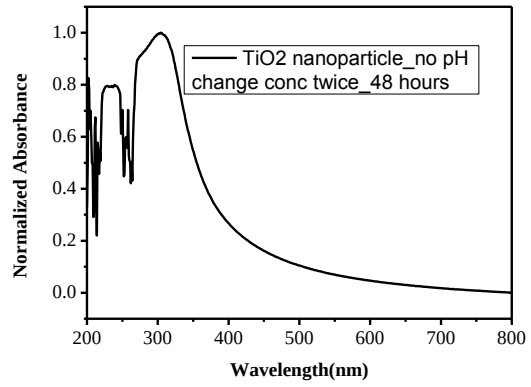

Figure 25: UV-Visible absorbance spectra.

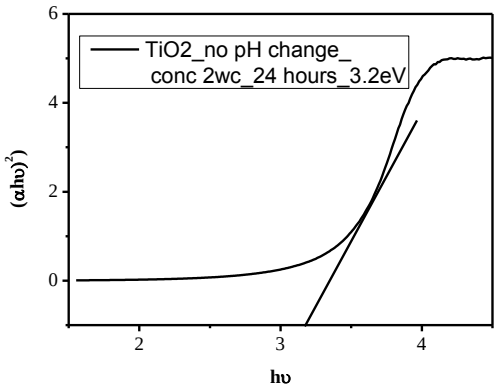

Figure 26: Tauc Plot, band gap 3.20 eV

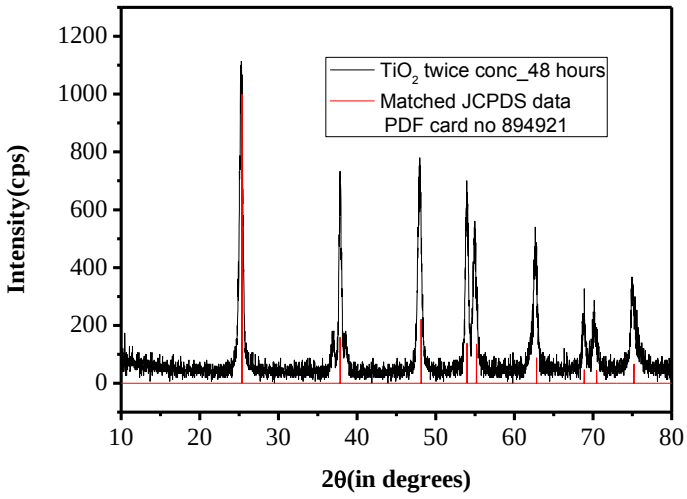

Figure 27: PXRD of TiO2 nanoparticle.
Matching with standard JCPDS PDF card (894921) the structure of TiO_2 nanoparticle is anatase phase and tetragonal crystal structure.

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data. UV-VIS spectroscopy was done and maximum wavelength was noted at 306 nm. Tauc plot was done and it gave the band gap to be 3.20 eV. The particle size was calculated using Debye-Scherrer formula for the planes (101), (004) and (200) respectively

and it gave size as 17.7 nm, 25.3 nm and 17.3 nm respectively. SEM and TEM images are yet to be taken and the actual particle size would be confirmed from that.

Experiment No. 7

Aim:-Synthesis of TiO_2 nanoparticle for solar cell application, keeping reaction time as 24 hours, no change in concentration, and no pH change.

Procedure:-

We followed the same procedure as in the case of the first experiment with one variation that is we kept the reaction time as 24 hours.

Characterization:-

The above prepared nanoparticles were characterized by UV-VIS spectroscopy.

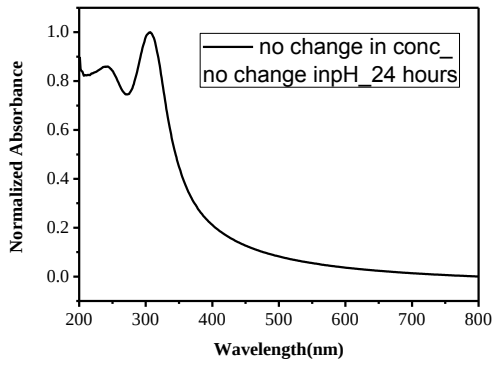

Figure 28: UV-Visible absorbance spectra.

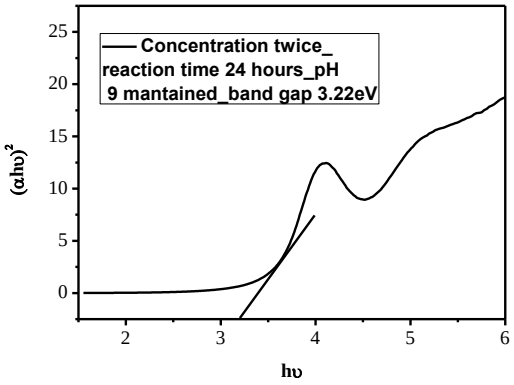

Figure 29: Tauc Plot, band gap 3.22 eV

Results:-

Titanium dioxide nanoparticles were synthesized and it was confirmed by XRD upon matching JCPDS data. UV-VIS spectroscopy was done and maximum wavelength was noted at 305 nm. Tauc plot was done and it gave the band gap to be 3.22 eV. The particle size was calculated using Debye-Scherrer formula for the planes (101), (004) and (200) respectively and it gave size as 15.1 nm, 25.6 nm and 18.0 nm respectively. SEM and TEM images are yet to be taken and the actual particle size would be confirmed from that.

Expt. No.	Counter Electrode	SILAR Treatment	No. Of Times
8	$MoSe_2$-Na_2S	No	0
9	H_2PtCl_6	No	0
10	H_2PtCl_6	Yes	2
11	H_2PtCl_6	Yes	2 and 4

Table 2: Experimental setup for experiment no. 8-11

Experiment No. 8

Aim:- To make Dye Sensitized Solar Cell, measure its short circuit current, open circuit voltage, fill factor, efficiency using FTO coated glass, TiO_2 paste of 20 nm size and using $MoSe_2$ and Na_2S mixture for ligand transfer and using the final solution as counter-electrode.

Procedure:-

FTO glass was cut in the appropriate dimensions and was carefully cleaned first with soap and then sonicated for 15 minutes. The same procedure is then followed using distilled water, acetone and ethanol. The FTO pieces are then kept in fridge. The FTO glass pieces are then taken out and dipped into 40 mM $TiCl_4$ solution in distilled water for 30 minute.(The 40 mM $TiCl_4$ solution was made by dissolving 1400 micro-litre 1M $TiCl_4$ into 35 ml water). There are two sides of the FTO coated glass, one is conducting that is the FTO coated side, while the other side is non-conducting and it is easily found out by using a multi metre. Marking is done on the side that is non-conducting. The FTO coated glasses are washed with distilled water and ethanol respectively and then left open for drying and then annealed in furnace at 500 °C for 30 minute. It is then taken out the next day.Taking the conducting side of the FTO upwards, a mask was prepared by the scotch tape so thatthe area inside remains approximately 1 cm x1cm. Then the TiO_2 paste was poured on to the edge side of the mask

and then it was spread by **doctor blading technique**(Doctor blading: a smooth glass rod spreads a viscous colloid on a glass surface (FTO) to a specific thickness with help of a tape frame, the solvent is thus evaporated and the tape is removed). This technique is repeated two times separately to make a 12 micrometre thickness to make it compatible with the dye to be used later, and then calcined at 500 °C for 30 minute. It is then taken out the next day. The second $TiCl_4$ electrode is again soaked in 40 mM $TiCl_4$ solution in distilled water for 30 minute and calcined it at 500 °C for 30 minute.It is then immersed into a 0.5 mM N719 dye solution (0.089 gram) in a mixed solvent of acetonitrile and tertiary butyl alcohol (1:1 volume ratio) for 20 h to absorb the dye onto the TiO_2 surface. The counter electrode is fabricated by the spin coating/drop casting of the ligand transferred solution of $MoSe_2$-Na_2S assembly. The assembly was made by dissolving 6 mg of $MoSe_2$ in 3 ml toluene, and then 15 mg of Na_2S in 3 ml form-amide. Then both the solutions were sonicated for full dissolution, and then the second solution was poured into the first one. Then the assembly was kept in magnetic stirrer for 24 hours to enable ligand exchange to take place. The two electrodes were sealed by heating and joining, and by applying pressure by fingertip, and then sandpaper treatment is done to decrease the added resistance due to the successive $TiCl_4$ treatments.Finally electrolyte is injected through hole between two electrodes. Electrolyte is comprised of 0.03 M I_2, 0.6 M BMII,0.5 M 4-tertbutylpyridine in a mixture of acetonitrile and Valero-nitrile in 85: 15 volume ratio.At last, the I-V characteristics are noted using Solar Simulator Model.

Characterization:-

The above prepared DSSC-QDSSC hybrid was characterized by Solar Cell Simulator.

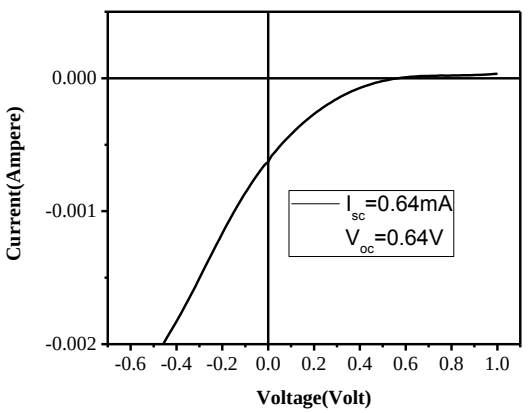

Figure 31: I-V characteristics of solar cell.

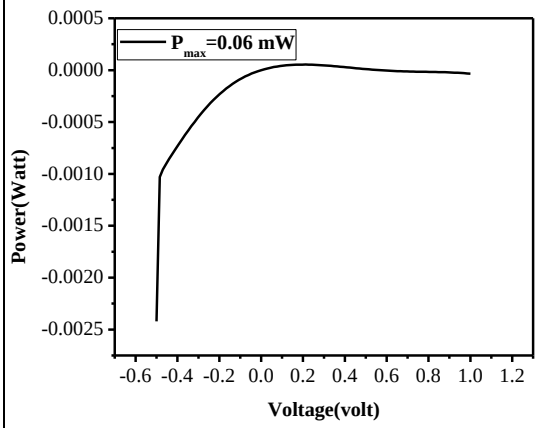

Figure 32: P-V characteristics of solar cell. Efficiency is 0.275 %

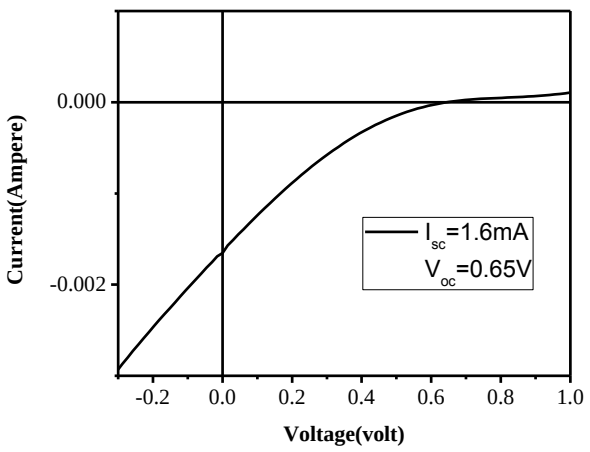

Figure 33: I-V characteristics of solar cell.

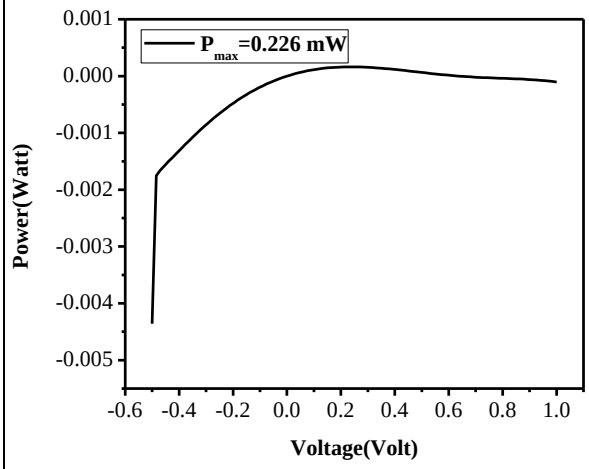

Figure 34: P-V characteristics of solar cell. Efficiency is 0.8 %

Results:-

1st cell:-

I-V characteristics were noted and it gave short circuit current of 0.64 mA and open circuit voltage as 0.64 V. The P-V graph was drawn and the maximum power was found out to be 0.226 mW. The efficiency was calculated to be 0.275 %.

2nd cell:-

I-V characteristics were noted and it gave short circuit current of 1.6 mA and open circuit voltage as 0.65 V. The P-V graph was drawn and the maximum power was found out to be 0.06 mW. The efficiency was calculated to be 0.8 %.

Experiment No. 9

Aim:- To make Dye Sensitized Solar Cell, measure its short circuit current, open circuit voltage, fill factor, efficiency using FTO coated glass, TiO_2 paste of 20 nm size and using H_2PtCl_6 solution as counter-electrode.At last, the I-V characteristics are noted using Solar Simulator Model.

Procedure:-

We followed nearly the same procedure as that of the first experiment. The only change that we made here was that of the counter electrode, that was made by the spin coating/ drop casting of 0.005M of H_2PtCl_6 solution.

Characterization:-

The above prepared DSSC was characterized by Solar Cell Simulator.

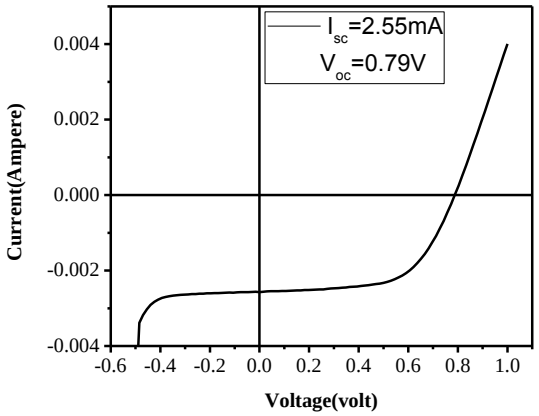

Figure 35: I-V characteristics of solar cell.

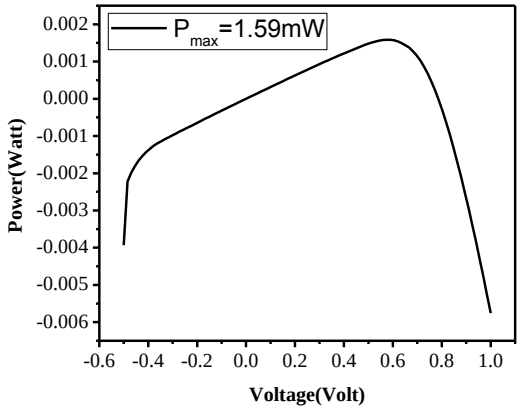

Figure 36: P-V characteristics of solar cell. Efficiency is 6.05 %

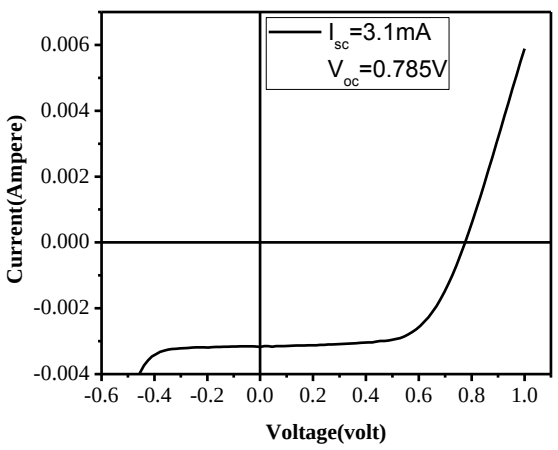

Figure 37: I-V characteristics of solar cell.

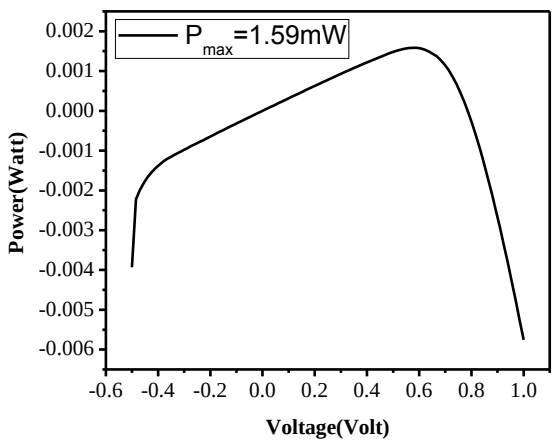

Figure 38: P-V characteristics of solar cell. Efficiency is 6.36 %

Results:-

1st cell:-

I-V characteristics were noted and it gave short circuit current of 3.1 mA and open circuit voltage as 0.785 V. The P-V graph was drawn and the maximum power was found out to be 1.59 mW. The efficiency was calculated to be 6.05 %.

2nd cell:-

I-V characteristics were noted and it gave short circuit current of 0.64 mA and open circuit voltage as 0.64 V. The P-V graph was drawn and the maximum power was found out to be 1.59 mW. The efficiency was calculated to be 6.36 %.

Experiment No. 10

Aim:- To make Dye Sensitized Solar Cell, measure its short circuit current, open circuit voltage, fill factor, efficiency using FTO coated glass, TiO_2 paste of 20 nm size, using H_2PtCl_6 as counter-electrode and using 2 times SILAR treated photo-anode.

Procedure:-

We followed nearly the same procedure as that of the first experiment. The changes that we made includes the SILAR treatment of the photo-anode. Two solutions, one 0.1M $CdNO_3$ and the other 0.1M Na_2SeSO_3 were prepared. The second solution was made more reactive by the addition of a reducing agent $NaBH_4$.The FTO coated glasses were then dipped first into the

cadmium nitrate solution for strictly 30 seconds, and then taken out and cleaned with distlilled water and ethanol respectively. The same procedure was repeated with the Na_2SeSO_3 solution that completed one round of SILAR treatment. We completed two rounds of SILAR treatment.The counter electrode is fabricated by the spin coating/drop casting of the prepared H_2PtCl_6 solution.At last, the I-V characteristics are noted using Solar Simulator Model.

Characterization:-

The above prepared DSSC was characterized by Solar Cell Simulator.

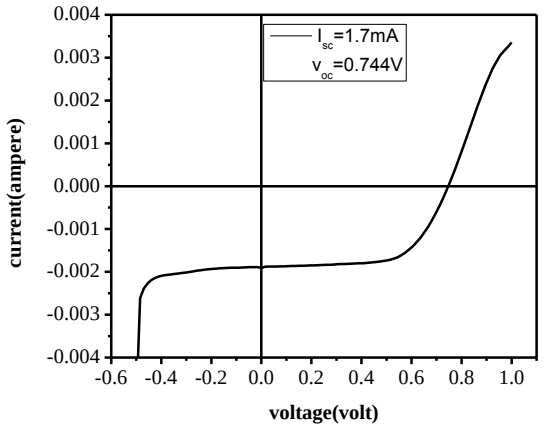

Figure 39: I-V characteristics of solar cell.

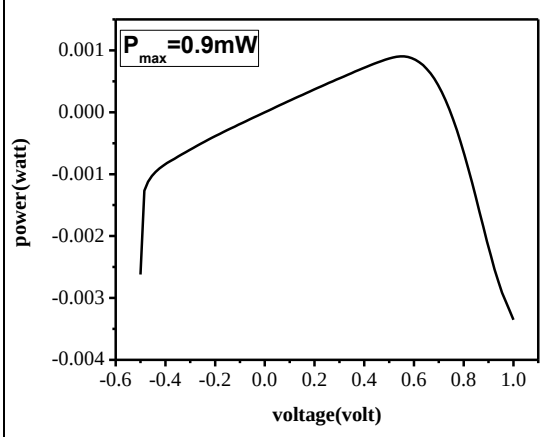

Figure 40: P-V characteristics of solar cell. Efficiency is 4.5 %

Results:-

I-V characteristics were noted and it gave short circuit current of 1.7 mA and open circuit voltage as 0.744 V. The P-V graph was drawn and the maximum power was found out to be 0.9 mW. The efficiency was calculated to be 4.5 %.

Experiment No. 11

Aim:- To make Dye Sensitized Solar Cell, measure its short circuit current, open circuit voltage, fill factor, efficiency using FTO coated glass, TiO_2 paste of 20 nm size and using H_2PtCl_6 as counter-electrode and using 2 times and 4 times SILAR treated photo-anode respectively.

Procedure:-

We followed nearly the same procedure as that of the first experiment. The changes that we made includes the SILAR treatment of the photo-anode. Two solutions, one 0.1M $CdNO_3$ and the other 0.1M Na_2SeSO_3 were prepared. The second solution was made more reactive by the addition of a reducing agent $NaBH_4$.The FTO coated glasses were then dipped first into the cadmium nitrate solution for strictly 30 seconds, and then taken out and cleaned with distlilled water and ethanol respectively. The same procedure was repeated with the Na_2SeSO_3 solution that completed one round of SILAR treatment. We completed two rounds of SILAR treatment.The counter electrode is fabricated by the spin coating/drop casting of the prepared H_2PtCl_6 solution.At last, the I-V characteristics are noted using Solar Simulator Model.

Characterization:-

The above prepared DSSC was characterized by Solar Cell Simulator.

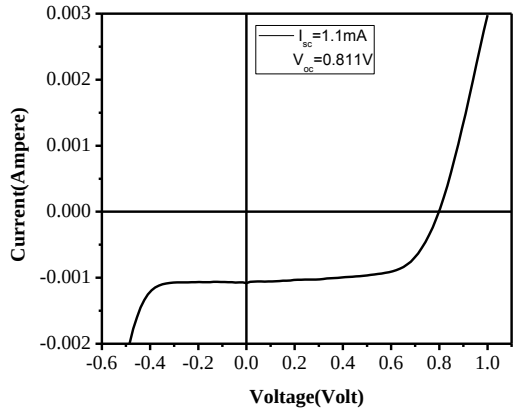

Figure 41: I-V characteristics of solar cell.

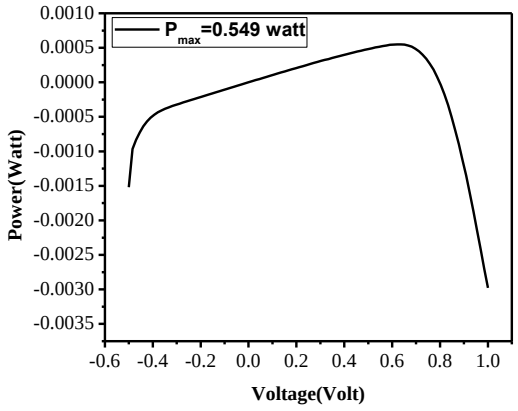

Figure 42: P-V characteristics of solar cell. Efficiency is 2.25 %

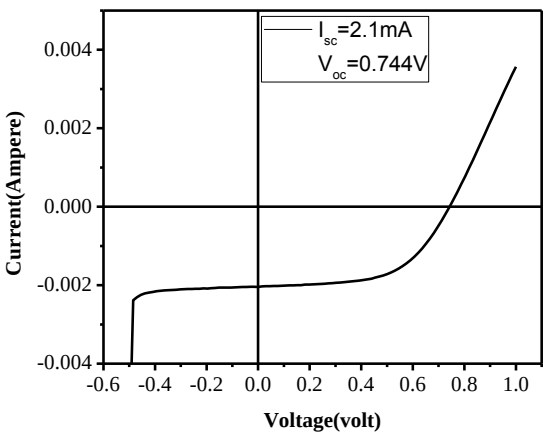

Figure 43: I-V characteristics of solar cell.

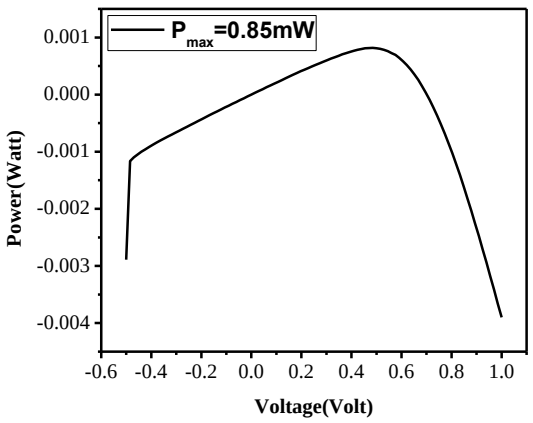

Figure 44: P-V characteristics of solar cell. Efficiency is 4.25 %

Results:-

1st cell:-

I-V characteristics were noted and it gave short circuit current of 1.1 mA and open circuit voltage as 0.811 V. The P-V graph was drawn and the maximum power was found out to be 0.549 mW. The efficiency was calculated to be 2.25 %.

2nd cell:-

I-V characteristics were noted and it gave short circuit current of 2.1 mA and open circuit voltage as 0.744 V. The P-V graph was drawn and the maximum power was found out to be 0.85 mW. The efficiency was calculated to be 4.25 %.

CONCLUSIONS

We synthesized TiO_2 nanoparticles by increasing the concentration of the reactants, pH of the solution, time of the reaction. Mostly the nanoparticles formed are in the anatase phase except the two reactions where we varied the concentration of the reactants and pH of the solution together, where we obtained a mixture of both rutile and anatase phase. In the case of changing pH of the solution, concentration of the reactants separately, we got red shifts in wavelength of them as compared to the set where no change was made, depicting an increase in particle size. The effect of increasing the concentration of the reactants and the pH of the solution at a time is negative as we observed a blue shift in their wavelengths, which depicts decrease in particle size.

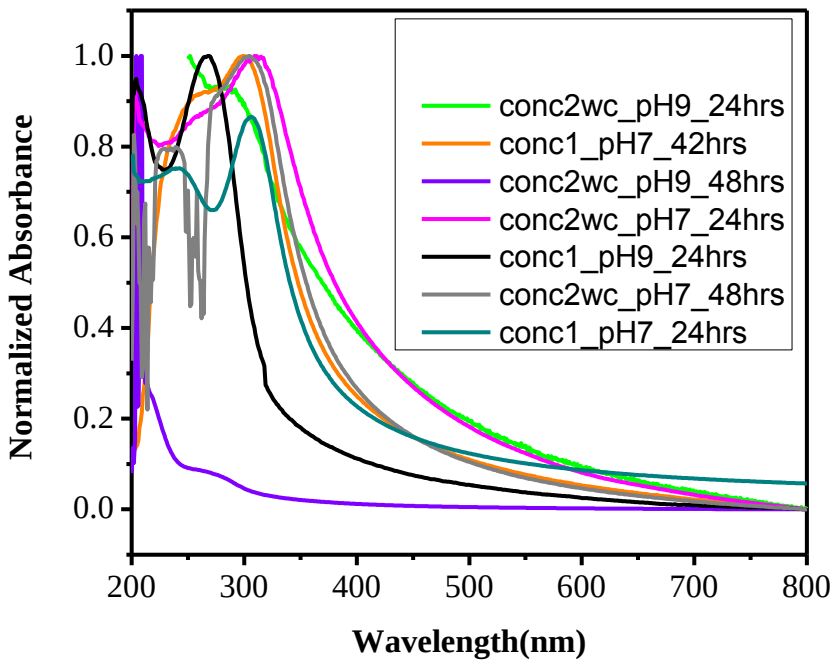

Figure 45: Comparative analysis of the maximum wavelength of the TiO_2 nanoparticles obtained from UV-VIS spectra, where the titanium dioxide nanoparticles were dissolved in ethanol.

The average sizes of the nanoparticles were calculated using Debye-Scherrer formula for the planes (100), (004) and (200) respectively where it depicts an increase in particle size when compared to the nanoparticle where no change was done, for the sets where pH change, concentration change were done separately. In cases of joint application, sizes were as less as 5 nm. The increase in reaction time had a minimal effect. TEM images were taken for the set

where only pH change was done with reaction continued for 24 hours. It gave particle size for that set to be around 40 nm, and this increase in particle size in accordance with the red shift seen in UV-VIS spectra.

We made a QDSSC-DSSC hybrid, but the efficiency came out a little bit low. We made DSSC with H_2PtCl_6 as counter electrode, and later made more DSSCs with 2 times and 4 times SILAR treated photo anode. We observed efficiencies of around 6-7 % in the DSSC made with H_2PtCl_6 as counter electrode, where in case of the SILAR treated DSSCs, efficiencies were little low than the former but we observed a voltage enhancement, and it is surprising.

FUTURE SCOPE

1. It is to be find out why there is a decrease in particle size when changes in pH and concentration were made together in one reaction, where there is an increase in particle size when these changes are deployed separately.
2. We can start our reaction by varying ratios of $TiCl_4$:H_2O[12] and that may prove crucial.
3. We may autoclave our solution at higher temperatures[13] as 300-400 degree Celsius to see its effect upon the size of the nanoparticle thus synthesized.
4. We can run our entire procedure of TiO_2 synthesis in sonication[14] and see its effect.
5. It is to be find out why there is a voltage enhancement upon SILAR treatment on photo anode in the case of DSSC made with H_2PtCl_6 as counter electrode.

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