

FINAL REPORT
Major Research Project

UGC F. No. 40-466/2011/ (SR), Dated: 30th June 2011 and
F. No. 40-466/2011/ (SR), Dated: 19th October 2012

Entitled
**“Dual Sensitization of Hydrothermally grown TiO₂ for
Efficient Solar Cells”**



Principal Investigator
Dr. H.P. Deshmukh
Associate Professor
YASHWANTRAO MOHITE COLLEGE
BHARATI VIDYAPEETH DEEMED UNIVERSITY,
PUNE (INDIA) – 411 038

Submitted to
UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG,
NEW DELHI -110 002

Year 1st July 2012 to 30th June 2015



**BHARATI VIDYAPEETH DEEMED UNIVERSITY,
YASHWANTRAO MOHITE COLLEGE PUNE- 411038**

FINAL REPORT

1st July 2012 to 30th June 2015

F. No. 40-466/2011/ (SR), Dated: 30th June 2011 and

F. No. 40-466/2011/ (SR), Dated: 19th October 2012

MAJOR RESEARCH PROJECT

Project Title

**“Dual Sensitization of Hydrothermally grown TiO₂ for
Efficient Solar Cells”**

Principal Investigator

Dr. H. P. Deshmukh

Associate Professor

Department of Physics

Yashwantrao Mohite College Pune – 411 038 (Maharashtra)

e-mail: hp_deshmukh@yahoo.com Contact No. : 09096044100

Submitted to

**THE SECRETARY
UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG,
NEW DELHI -110 002**

Tenure : July 2012 to June 2015



BHARATI VIDYAPEETH DEEMED UNIVERSITY, PUNE

(Established u/s 3 of the UGC Act, 1956 vide Notification No. F.9-15/95-U.3 of the Government of India)

YASHWANTRAO MOHITE COLLEGE OF ARTS, SCIENCE & COMMERCE

Founder-Chancellor :
Dr. Patangrao Kadam
M.A., LL.B., Ph.D.

Principal :
Dr. K. D. Jadhav
M.Sc., M.Phil., Ph.D.

Erandwane, Pune - 411 038

★ 'A' Grade University Status by MHRD, Govt. of India ★
★ Accredited & Reaccredited with 'A' Grade by NAAC ★

Tel. : (020) 25433383, 25424163
Fax : (020) 25440201
E-mail : bvdumc@hotmail.com
ymc@bharativedyapeeth.edu
Website : ymc.bharativedyapeeth.edu

Ref. No. BVDU/YMC/UGC/ /2015-2016

Date: 21/02/2016

To,
The Secretary,
University Grants Commission,
Bahadur Shah Zafar Marg,
New Delhi-110002.

**Sub: Submission of Final report of Major Research Project (F. No. 40-466/2011/(SR)
of Dr. H. P. Deshmukh Associate Professor in Physics.**

Sir/Madam,

We are pleased to forward the final report of Major Research Project in Physics (Science), as referred above, completed by Dr. H. P. Deshmukh, Associate Professor, Department of Physics, Y. M. College, Pune entitled **"Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"**.

Please find enclosed

1. Audited Utilization Certificate
2. Statement of Expenditure and Annexure
3. Summary of final report
4. Head wise audited statement of accounts
5. Total dues to be reimbursed by UGC, Delhi, Amounting totally Rs. 6,44,333/-
(In words – Six lakh forty four thousand three hundred thirty three only)

You are cordially requested to approve the amount and arrange to send (a) second and final installment (Rs. 2,86,500/-) (b) revised fellowship difference (Rs. 2,40,000/-) (c) HRA @ 20% of the fellows (Rs. 1,05,600/-) as detailed in the certificate attached and (d) an excess expenditure incurred i.e. Rs.12,233/-. Total amount is **Rs. 6,44,333/-** (Rs. Six lakh forty four thousand three hundred thirty three only). So please approve the same and arrange to send the amount at an early date and oblige.

Thanking you.

Dr. H. P. Deshmukh,
Principal Investigator

Yours faithfully,

(Prin. K. D. Jadhav)

PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038.**

FINAL REPORTS

Major Research Project in Physics

Project Title: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

Principal Investigator : Dr. H. P. Deshmukh

Acknowledgements

Major Research Project in Physics has been successfully completed and good achievements have been obtained. In this respect I take this opportunity to express my hearty thanks to **University Grants Commission**, New Delhi, for the sanction of this project and relieving the grants. I am very much thankful to respected Hon'ble Dr. S. S. Kadam, Vice Chancellor, Bharati Vidyapeeth Deemed University, Pune, for his valuable guidance.

I would like to thanks all the staff members of Y. M. College, Erandwane, Pune for their support and encouragement during the period. Furthermore I would like to thank all my colleagues for their helping hands in every respect.

A special word of thanks should be given to all the staff members of Physics Department, University of Pune for their kind support given to me. I am also thankful to C-Met, Pune and University of Pune for the support given in analysis of the samples.

I thank to Mr. Sudhir Vavale, Project Fellow who handle the project very sincerely and carefully during the project tenure.

I thank to Mr. Ashok Koli, Accountant for maintaining accounts, Mr. Tanaji Kadam, for departmental assistance

Last but not the least; I would like to thank my parent and family members for their kind help, cooperation and encouragement at every moment.

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038.**

FINAL REPORTS

Major Research Project in Physics (Science)

Project Title: "Dual Sensitization of Hydrothermally grown TiO_2 for Efficient Solar Cells"

Principal Investigator : Dr. H. P. Deshmukh

DEDICATION

Whole Heartedly Dedicated to

Prof. Dr. Shivajirao S. Kadam

Vice Chancellor

Bharati Vidyapeeth University, Pune (India)

UNIVERSITY GRANTS COMMISSION

BAHADUR SHAH ZAFAR MARG

NEW DELHI – 110002

FINAL REPORT

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038.**

Major Research Project

1st July 2012 to 30th June 2015

File No. 40-466/2011 / (SR), Dated: 30th June 2011 and

F. No. 40-466/2011 / (SR), Dated: 19th October 2012

Title: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

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Annexure-III

**UNIVERSITY GRANT COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110002.**

**Final Report of the work done During the Major Research Project in Physics (Science)
1st July 2012 to 30th June 2015**

**Ref. : Major Research Project_ (F. No. 40-466/2011/ (SR), Dated: 30th June 2011 and
F. No. 40-466/2011/ (SR), Dated: 19th October 2012)**

S.N.	Description	Details
1.	Project report No.	Final report
2.	UGC Reference No.	F. No. 40-466/2011/(SR), Dated: 30 th June 2011 & F. No. 40-466/2011/(SR), Dated: 19 th October 2012
3.	Period of report	1 st July 2012 to 30 th June 2015
4.	Title of research project	Dual Sensitization of Hydrothermally grown TiO ₂ for Efficient Solar Cells
5.	(a) Name of the Principal Investigator	Dr. H.P. Deshmukh
	(b) Department and University/College where work has progressed	Department of Physics, Yashwantrao Mohite College, Bharati Vidyapeeth Deemed University, Erandawane, Pune-411038.
6.	Effective date of starting of the project	01 - 07 - 2012 to 30 - 06 - 2015
7.	Grant approved and expenditure incurred during the period of the project	Annexure - V
	(a) Total amount approved Rs.	8,75,800/-
	(b) Amount received 1st installment	5,89,300/-
	Total expenditure	8,88,033/-
	(i) Balance Receivable 2 nd Installment	2,86,500/-
	(ii) difference of revised rate of project fellowship from 2012 onwards	(1,44,000 for 1 st & 2 nd yr. @ 6000 p.m. & 96,000 for 3 rd yr. @ 8000 p.m.) = 2,40,000/-
	(iii) + HRA @20% for 1 st & 2 nd yr. on Rs, 14,000/- (2800/- pm) & 3 rd yr. on 16,000/- (3200/-pm)	67,200 + 38,400 = 1,05,600/-
	Excess Amount	12,233/-
	Total dues to be receivable from UGC (i+ii+iii+iv)	2,86,500+2,40,000+1,05,600+12,233 = 6,44,333/-
8.	Report of the work done:	
	(i) Brief objective of the project	See on page No. 8
	(ii) Work done so far and results achieved and publications, if any, resulting from the work	Final report and annexure - VII and VIII. See on page No. 9

(i) Objectives

- 1) To fine tune the process parameters to deposit good quality thin films of TiO_2 nanostructures by hydrothermal technique.
- 2) Optimization and development of Dye Sensitized Solar Cell (DSSC) with TiO_2 nanostructures and quantum dot solar cells.
- 3) Synthesis and characterization of the TiO_2 thin films for structural, morphological, and optical properties like X-ray diffraction (XRD), energy dispersive X-ray microanalysis (EDX), Scanning electron microscopy (SEM), Field emission Scanning electron microscopy (FESEM) transmission electron microscopy (TEM), and UV-Visible spectrophotometer and FT-IR technique etc.
- 4) Optimization and development of CdS sensitized TiO_2 nanostructures for solar cells
- 5) Optimization and development of dye and CdS sensitized (dual sensitized) TiO_2 nanostructures for solar cells
- 6) To characterize the CdS-dye- TiO_2 thin films for structural, morphological, and optical properties like X-ray diffraction (XRD), energy dispersive X-ray microanalysis (EDX), Field emission Scanning electron microscopy (FESEM) and UV-Visible spectrophotometer and FT-IR technique.
- 7) To characterize thin films for their solar cells properties such as, current-voltage (I-V), Incident photo-to-current conversion efficiency (IPCE). The efficiency of prepared solar cells were estimated through I-V characterization measured with a Keithley 2400 source meter using an AM 1.5 (100 mW/cm^2) solar simulator.
- 8) Fabrication of DSSCs based on these complementary combination and study of their performance
- 9) Sensitization of TiO_2 electrode with a Standard ruthenium-complex N719 dyes. Post treatment are carefully controlled and optimized.
- 10) Synthesis of the CdS Quantum Dots on oxide surface by Successive Ionic Layer Adsorption and Reaction (SILAR) Method.

(ii) Publications, if any, resulting from the work

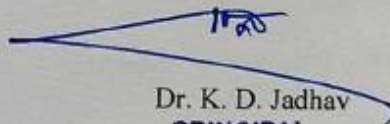
Five (05) research papers have been published in the international journal and conferences.

- 1) Hydrothermal synthesis of rutile TiO₂ bottle brush for efficient dye-sensitized solar cells
Journal of nanoparticle research 16 – 6 (2014) 1 – 11
- 2) Characterization of TiO₂ thin films deposited by hydrothermal method.
2nd International Conference on “Physics of Materials and Materials Based Device Fabrication – (ICPM-MDF-2014)” 13th –15th January 2014
Department of Physics, Shivaji University, Kolhapur, Maharashtra.
- 3) Synthesis and characterization of hydrothermally grown CdS Sensitized TiO₂ for quantum dot solar cells.
International Photovoltaic Solar Energy Conference (IPSEC) SOLAR ASIA - 2015
30th July – 1st August, 2015, Department of Physics Savitribai Phule Pune University, pune, Maharashtra.
- 4) Synthesis and Characterization of TiO₂ thin films on FTO by hydrothermal process.
Raman Memorial Conference (2015) 13th –14th February 2015
Department of Physics, Savitribai Phule Pune University, pune, Maharashtra.
- 5) One paper entitled ‘Nanocrystalline Flowers of Rutile TiO₂ Synthesized By Hydrothermal Method’ is submitted to journal named “Bulletin of Materials Science” (manuscript Draft is attached at the end of the report)
Thus the project is successfully completed.

9.	(iii) Has progress been according to original plan of work and towards achieving the objective?	Yes, the progress has been according to the original plan of work and towards achieving the objectives.
	(iv) Please indicate the difficulties, if any, experienced in implementing the project	(a) For the analysis of sample and their interpretation extra time was required because these facilities were availed from outside institutes. (b) First project fellow was irresponsible & did not cooperate properly. So I had to change the 1 st project fellow and due to marriage the 2 nd project fellow left the job.
	(v) If project has not been completed, Please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the Commission on a separate sheet	-----
	(v) If the project has been completed, please enclose a summary of the findings of the study. Two bound copies of the final report of work done may also be sent to the Commission	The project has been completed; the summary of the project has been enclosed in the final report (Page No. 104)
	(vi) Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any	One man trained during complete project Enrolled Ph. D. attached registration letter. Attached in annexure VII ----



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

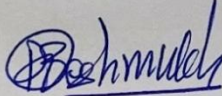
Annexure - IV

M/S V. A. Dudhedia & Co.
Chartered Accountants,
CTS No. 1249150, Good Luck Chowk
Deccan Gymkhana, Pune - 411004.
Office: 020-25531717 / 25531718.

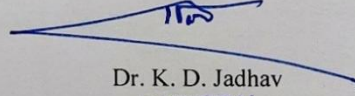
UTILIZATION CERTIFICATE

This is certified that the Total grant of Rs. 8,75,800/- (Rupees Eight Lakh Seventy Five Thousand Eight Hundred Only) has been sanctioned for the Major Research Project in Physics (Science) to Dr. H. P. Deshmukh, entitled "**Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells**" by the University Grants Commission vide their letter no. F. No. 40-466/2011/ (SR), Dated: 30th June 2011 and F. No. 40-466/2011/ (SR), Dated: 19th October 2012. Out of which, the 1st installment of Rs. 5,89,300/- (Rs. Five Lakh Eighty Nine Thousand Three Hundred Only) has been received. Total expenditure incurred for implementation of the said project is Rs. 8,88,033/- (Rs. Eight Lakh Eighty Eight Thousand Thirty Three only). Dues towards UGC are 2nd installment to be received i.e. Rs. 2,86,500/- + Excess Expenditure Rs. 12,233/- and revised fellowship difference + 20% HRA Rs. 3,45,600/- totally amounting to Rs. 6,44,333/- (Rs. Six lakh forty four thousand three hundred thirty three only). Terms and conditions have been fulfilled by the college and the grant has been fully utilized for the purpose for which it was sanctioned in accordance with the terms and conditions laid down by the UGC.

You are cordially requested to release the remaining amount of Rs. 6,44,333/- (In words - Rs. Six lakh forty four thousand three hundred thirty three only) at the earliest and oblige.



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.



M/S V.A. Dudhedia
Auditor Chartered Accountant

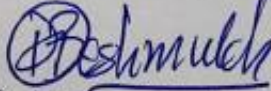
VIJAYKUMAR A. DUDHEDIA
CHARTERED ACCOUNTANT
M NO 13989

STATEMENT OF EXPENDITURE: 1st July 2012 to 30th June 2015
Major Research Project

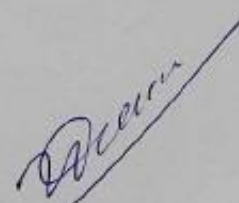
F. No. 40-466/2011/ (SR), Dated: 30th June 2011 and
F. No. 40-466/2011/ (SR), Dated: 19th October 2012

Title: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

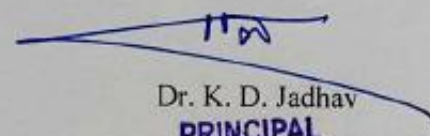
S. N.	Items	Amount Sanctioned	1 st installment	Amount Spent	Amount Balance	Excess Amount Spent	Remark
A	Non -Recurring						
1.	Books & Journals	---	---	---	---	---	---
2.	Equipments	2,50,000	2,50,000	2,27,836	22,164	---	Used 22,164/- for Chemicals Glassware/ Consumable
B	Recurring						
1.	Project fellow @ 8000/- P.M.	2,88,000	3,39,300	2,93,023	---	5,023	---
2.	Chemical/Glassware/ Consumable	1,50,000		2,03,697	---	53,697	---
3.	Hiring Services	---		---	---	---	---
4.	Contingency	90,000		69,470	20,530	---	Used 20,530/- for Chemicals Glassware/ Consumable
5.	Travel/Field Work	45,000		41,207	3,793	---	used 3,793/- for Chemicals
6.	Overhead charges	52,800		52,800	---	---	---
7.	Total (A+B)	8,75,800	5,89,300	8,88,033	46487	58,720 - 46487 = 12,233	---
Excess Expenditure						12,233	


Dr. H. P. Deshmukh
Principal Investigator




M/S V.A. Dudhedia
Auditor Chartered Accountant

VIJAYKUMAR A. DUDHEDIA
CHARTERED ACCOUNTANT
M No 13980


Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038.**

Major Research Project

1st July 2012 to 30th June 2015

File No. 40-466/2011 / (SR), Dated: 30th June 2011 and

F. No. 40-466/2011 / (SR), Dated: 19th October 2012

Project Title: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

CHANGE OF A/C HEADS DURING SPENDING THE AMOUNT

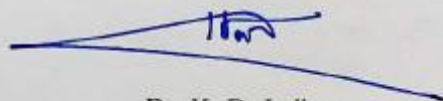
As the two research fellows have left their duties in between and third fellow completed the work but during these changes every fellow has wasted the chemicals for film deposition and some chemicals have been additionally wasted during optimization of films for obtaining good quality films. By that time the prices of chemicals were increased. For guaranteed purity of chemicals, we had to use imported (more costly) chemicals as it was strictly unavoidable. Hence more amount has been spent on chemicals. For this purpose we saved some amount from contingency (Rs. 20530/-) , travel (Rs 3793/-) and equipments (Rs 22164/-) totally amounting to Rs 46487/-. One instrument named 'double distillation water plant' of cost about Rs 34,000/- was not purchased and double distilled water for solutions was brought from other colleges and departments. The expenditure for chemicals was unavoidable and essential. Hence you are cordially requested to approve the same as per change of A/C heads as mentioned in the accounts and oblige.

Thanking you,

Yours faithfully,



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

M/S V. A. Dudhedia & Co.
Chartered Accountants,
CTS No. 1249150, Good Luck Chowk
Deccan Gymkhana, Pune - 411004.
Office: 020-25531717 / 25531718.

Major Research Project

1st July 2012 to 30th June 2015

File No. 40-466/2011 / (SR), Dated: 30th June 2011 and
F. No. 40-466/2011 / (SR), Dated: 19th October 2012

Title: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

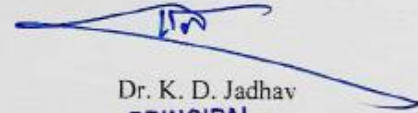
STATEMENT OF INCOME AND TOTAL EXPENDITURE INCURRED

S. No.	Agency	Amount sanctioned	Amount Released	Expenditure Incurred in Rs.
1.	UGC New Delhi	8,75,800/-	5,89,300/-	5,89,300/-
2.	Grant Receivable from UGC	2,86,500/-	---	2,86,500/-
3.	Total Expenditure	---	---	8,88,033/-
	Total Dues towards UGC	---	---	2,98,733/-

You are cordially requested to release the remaining amount of Rs. 2,98,733/- + Revised fellowship difference and 20% HRA Rs. 3,45,600.00 = 6,44,333/- at the earliest and oblige.

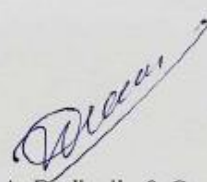


Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.




M/S V. A. Dudhedia & Co
Chartered Accountant

VIJAYKUMAR A. DUDHEDIA
CHARTERED ACCOUNTANT
M. No. 13989

BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038.

Final Report

1st July 2012 to 30th June 2015

File No. 40-466/2011 / (SR), Dated: 30th June 2011 and

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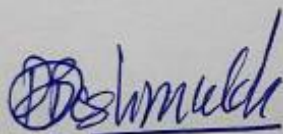
Tenure: 03 years

Major Research Project

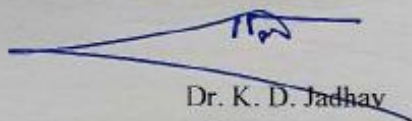
Project Title: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

CERTIFICATE OF UTILIZATION OF OVERHEAD CHARGES

Certified that the overhead charges of the project amounting to Rs. 52,800/- (In words Rupees Fifty Two Thousand Eight Hundred only) have been fully utilized for the purpose for which it was sanctioned in accordance with UGC norms.



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

Annexure - V

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002**

**STATEMENT OF EXPENDITURE IN RESPECT OF
MAJOR RESEARCH PROJECT**

1. Name of Principal Investigator : Dr. H. P. Deshmukh
2. Dept. of University/College : Yashwantrao Mohite College, Bharati Vidyapeeth
University, Pune - 411038
3. UGC approval No. and Date : F. No. 40-466/2011/(SR), Dated: 30th June 2011 and
F. No. 40-466/2011/(SR), Dated: 19th October 2012
4. Title of the Research Project : "Dual Sensitization of Hydrothermally grown TiO₂
for Efficient Solar Cells"
5. Effective date of starting the : 1st July 2012
project
6. a. Period of Expenditure : 1st July 2011 to 30th June 2015
b. Details of Expenditure : Given as below

Summary of the Expenditure

Sr. No.	Items	Amount Approved Rs	Grant released as 1 st installment	Expenditure Incurred Rs.
A	Non -Recurring			
1.	Books & Journals	--	--	--
2.	Equipments	2,50,000/-	2,50,000/-	2,27,836/-
B	Recurring			
3.	Project fellow @ 8000/- P.M.	2,88,000/-	3,39,300/-	2,93,023/-
4.	Chemical/Glassware/ Consumable	1,50,000/-		2,03,697/-
5.	Hiring Services	---		---
6.	Contingency	90,000/-		69,470/-
7.	Travel/Field Work	45,000/-		41,207/-
8.	Overhead charges	52,800/-		52,800/-
9.	Total (A+B)	8,75,800/-	5,89,300/-	8,88,033/-

(In words - Rs. Eight lakh eighty eight thousand thirty three only)

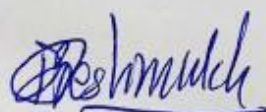
- c. Staff Project Fellow
d. Date of Appointment 11-10-2011

Sr. No.	Approved Rs. 8000/-	From to Period (36 Months)	Expenditure incurred Rs.	As per revised rate amount receivable + 20% HRA (Rs)
1.	2,88,000/-	11-10-2011 to 31-12-2014	2,93,023/-	3,45,600/-

- i. Difference of revised rate of project fellowship from 2012 onwards - (1,44,000 for 1st & 2nd yr. @ 6000 pm & 96,000 for 3rd yr. @ 8000 pm) = **2,40,000/-**
ii HRA @ 20% for 1st & 2nd yr. on Rs. 14,000/- (2800/- p.m.) & 3rd yr. on 16,000 (3200/- p.m.) = 67,200 + 38,400 = **1,05,600/-**
iii For Project Fellow, total receivable amount towards UGC
Rs. 2,40,000+1,05,600 = **3,45,600/-**

For details attached annexure-VI for Project Fellow amount

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.
2. It as a result of check or audit objective, some irregularity is noticed, later date, action will be taken to refund, adjust or regularize the objected amounts.
3. Payment @ revised rates shall be made with arrears on the availability of additional funds.
4. It is certified that the grant of Rs. 5.89,300/- **1st installment** (Rupees Five Lakh Eighty Nine Thousand and Three Hundred only) received from the University Grants Commission (total sanction amount 8,75,800/-) under the scheme of support for Major Research Project entitled "**Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells**" vide UGC letter No. File No. 40-466/2011/(SR), Dated: 30th June 2011 and F. No. 40-466/2011/(SR), Dated: 19th October 2012 has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

Annexure - VI

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038**

MAJOR RESEARCH PROJECT

F. No. 40-466/2011/(SR), Dated: 30th June 2011
F. No. 40 -466/2011/(SR), Dated: 19th October 2012
(1st July 2012 to 30th June 2015)

**TITLE OF THE PROJECT: "Dual Sensitization of Hydrothermally grown TiO₂ for
Efficient Solar Cells"**

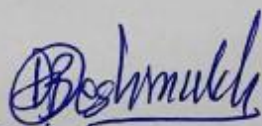
STATEMENT OF DUES OF PROJECT FELLOWS

Sr.No.	Years	Present Fellowship	Revised Fellowship	Arrears
1.	First Two years	8000/- p/m	14,000/- p/m	24 x 6,000 = 1,44,000/-
2.	Third year	8000/- p/m	16,000/- p/m	12 x 8,000 = 96,000/-
			Total	2,40,000/-

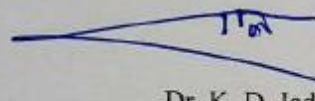
HRA @ 20%

Sr.No.	Years	HRA	Amount
1.	First Two years	20% of 14000/- = 2800/-	24 x 2800 = 67,200/-
2.	Third year	20% of 16000/- = 3200/-	12 x 3200 = 38,400/-
		Total	1,05,600/-

**Total dues of project fellows are Rs. 2,40,000/- + 1,05,600/- = 3,45,600/-
(In words Rs. Three lakh forty five thousand six hundred only)**



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038**

MAJOR RESEARCH PROJECT

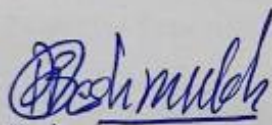
F. No. 40-466/2011 (SR), dated: 19th October 2012

F. No. 40-466/2011 (SR), dated: 30th June 2011

TITLE OF THE PROJECT: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

CERTIFICATE FOR CLAIM OF ARREARS OF PROJECT FELLOW

Certified that the claim of difference (arrears) of Project fellow during the three years. As per the UGC XI Plan the fellowship amount remaining for the first two years difference @ Rs. 6000/- per month for 24 month amounting to $6,000 \times 24 = 1,44,000/-$ (Rs. One Lakh Forty four Thousand) and for the third year difference Rs. 8,000 $\times 12 = 96,000/-$ (Rs. Ninety Six thousand). So total amounting **Rs. 1,44,000 + 96,000 = 2,40,000/- (Rs. Two Lakh Forty thousand only)** dues towards UGC New Delhi. It may be released at the earliest and oblige.



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

**BHARATI VIDYAPEETH DEEMED UNIVERSITY
YASHWANTRAO MOHITE COLLEGE, PUNE - 411038**

MAJOR RESEARCH PROJECT

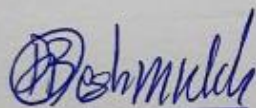
F. No. 40-466/2011 (SR), dated: 19th October 2012

F. No. 40-466/2011 (SR), dated: 30th June 2011

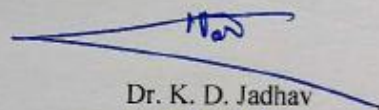
PROJECT TITLE: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

CERTIFICATE FOR CLAIM OF HRA OF PROJECT FELLOW

Certified that the claim of House Rent Allowances for the project fellows during three years. As per the UGC XI plan rules the fellowship for first two years of Rs. 14,000/- per month @ 20 % amount to $2860 \times 24 = 67,200/-$ (Rs. Sixty Seven Thousand Two Hundred only) and third year of Rs.16,000/- per month @ 20% amount to $3200 \times 12 = 38,400/-$ (Rs. Thirty eight Thousand Four Hundred only). So the total amount **Rs. 67,200 + 38,400 = 1,05,600/- (One Lakh Five Thousand Six Hundred Only)** may be released at the earliest and oblige.



Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

Annexure - VIII

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002**

MAJOR RESEARCH PROJECT

**PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF
SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT**

1.	Name and Address of the Principal Investigator	Dr. H. P. Deshmukh Associate Professor, Department of Physics, Yashwantrao Mohite College, Pune - 411038
2.	Name and Address of the institution	Yashwantrao Mohite College, Bharati Vidyapeeth University, Pune.
3.	UGC Approval No. and Date	F. No. 40-466/2011/(SR), Dated: 30 th June 2011 and F. No. 40-466/2011/(SR), Dated: 19 th October 2012
4.	Date of Implementation	01/07/2012
5.	Tenure of the Project	1 st July 2012 to 30 th June 2015
6.	Total Grant Allocated	8,75,800/-
7.	Total Grant Received	5,89,300/-
8.	Final Expenditure	888033/-
9.	Title of the Project	"Dual Sensitization of Hydrothermally grown TiO ₂ for Efficient Solar Cells"
10.	Objectives of the Project	Attached in Final report Page No.8
11.	Whether Objectives were achieved (Give details)	Yes, details are in final report copy
12.	Achievements from the Project	<ul style="list-style-type: none">• The structural properties were studied and it proved to be a stable at higher temperature.• This work brings us one step closer to a fully renewable energy source.• Environmentally friendly Dye sensitized solar cell• Although the present work is primarily experimental, multiscale thinking can provide valuable direction for the DSSC and quantum dot solar cell.• Industrially important solar cell due to its low cost.• Minimize environmental pollution.• These results may be useful for further progress in the field of solar cells (photovoltaic devices).
13.	Summary of the Findings	See on next page (Page No. 22)

SUMMARY OF THE FINAL REPORT

The solar cell technology is not new but the kind of work undertaken by us is to fabricate low cost, higher conversion efficiency and stable solar cells. Hence our one of the objectives is to use cost-effective and low temperature method like hydrothermal technique to grow high quality TiO_2 and CdS-TiO_2 thin films for solar cells device application.

Dye sensitised solar cells (DSSCs) are being developed and studied by magnetron sputtering, spray pyrolysis, e-beam evaporation and similar physical vapor deposition techniques. But If the deposition of TiO_2 is made by simple hydrothermal method, then the manufacturing cost of solar cell materials should be lower than that of materials deposited by vacuum deposition process

Nanotechnology can provide many benefits to photovoltaic (solar cell) applications by combining novel nanoscale properties with low cost. Nanorods or nanowires are interesting because they have a long axis to absorb incident sunlight.

The addition of CdS to array of nanorods improves light harvesting by adding more material to absorb incident light. These nanostructures have large area that harvest solar light and cause increased scattering that improves light absorption. It is necessary to develop simple and cost effective devices to improve power conversion efficiency of solar cells without sacrificing its long term stability.

The visible band gap semiconductor sensitization is the best option to improve power conversion efficiency. The semiconductor nanoparticles were used to protect the surface of TiO_2 , which ultimately increases the performance of the DSSCs. This approach provides an effective linkage between dye molecules and TiO_2 surface. By embedding CdS nanoparticles between the TiO_2 and dye molecules, the surface aggregation can be prevented.

The proposed work is related to the development of DSSC, based on TiO_2 and $\text{TiO}_2\text{-CdS}$ nanostructures. Once the dual sensitized devices are made stable under sunlight then efforts will be made to increase the efficiency.

Composites of TiO_2 with other in-organic materials proved to enhance power conversion efficiency. All DSSCs devices, based on CdS , CdSe , thin films were developed to improve stability of the devices. It was found that the CdS nanoparticles could improve the solar cells performance of the TiO_2 film greatly. The experimental results indicate that the absorbance of the thin film was increased after the nanoparticle sensitization.

In the field of solar cells, one of the great strengths of TiO_2 is the ability to tailor the DSSC properties via modification of the structure. It exhibit large band gap, fast electron transportation which are useful in DSSC device technology.

Different process parameters associated with both these techniques like film thickness, precursor concentration, deposition time and temperature etc. will be carefully optimized.

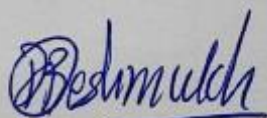
The thin films were characterized using Fourier transform infra-red spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Energy dispersive x-ray analysis (EDS), x-ray photoelectron spectroscopy (XPS) etc. techniques. Photo-Electrochemical applications were studied by using current-voltage (I-V), Incident photo-to-current conversion efficiency (IPCE).

TiO₂ nanoflowers were deposited by hydrothermal method. Then we use the simple SILAR sensitization process to deposit CdS quantum dots on TiO₂ nanoflowers. We described the calculation of the light harvesting ability of TiO₂ nanoflowers coated with quantum dots. The TiCl₄ treatment on TiO₂ nanoflowers films enhanced the performance of resulting DSSCs. TiO₂ nanoflowers film sensitized with N719 dye enhanced a power conversion efficiency from 1.98% to 2.73 %.

It is found that TiO₂ bottle brush provides effective large surface area which is much higher than that of TiO₂ nanorods or TiO₂ nanoflowers. Hence it improves the dye absorption and photovoltaic performance of DSSCs. A best power conversion efficiency of 6.63% has been achieved in case of TiO₂ bottle brush.

14.	Contribution to the Society	<ol style="list-style-type: none"> 1. Solar cells are renewable energy source therefore it is sustainable and will never run out. 2. Solar cells require less maintenance than traditional generators. 3. Their fuel being derived from natural and available resources, reduces the costs of operation so industrially important 4. No pollution is produced, so has minimal impact on the environment.
15.	Whether any Ph.D. Enrolled/ Produced out of the Project	One project fellow is enrolled for Ph. D. Registration letter is attached at the end.
16.	No. of Publications out of the Project	<ol style="list-style-type: none"> 1) Electrochromic performance of the mixed V₂O₅-WO₃ thin films synthesized by pulsed spray pyrolysis technique <u>Current Applied Physics</u>; 14 - 3 (2014) 389-395 2) Development of Zn₂SnO₄ thin films deposited by spray pyrolysis method and their utility for NO₂ gas sensors at moderate operating temperature

	<p><u>Journal of Analytical and Applied Pyrolysis</u>; 107 (2014) 233-241</p> <p>3) Functionalized Multi-Walled Carbon Nanotubes for Nitrogen Sensor <u>Journal of Applied Chemistry</u> 7 -11 (2014) 49-52</p> <p>4) Studies on an antimicrobial activity of metal (Mn, Fe, Co, Ni, Cu) chelates of 1, 2-naphthoquinone 2-oxime <u>International Journal of Chemical Sciences</u> 11- 3 (2013) 1286-1298</p> <p>5) Electrochromic properties of vanadium oxide thin films prepared by PSPT: Effect of substrate temperature <u>AIP Conference Proceedings</u> 1536 (2013) 517-518</p> <p>6) Farming of ZnO nanorod-arrays via aqueous chemical route for photoelectrochemical solar cell application <u>CERAMICS INTERNATIONAL</u> 38 - 8 (2012) pp. 6461-6467</p> <p>7) Enhanced electrochromic performance of f-MWCNT-WO₃ composite <u>Electrochimica Acta</u> 58-1 (2011) 556-561</p> <p>8) Electrochromic performance of mixed V₂O₅-MoO₃ thin films synthesized by pulsed spray pyrolysis technique <u>Materials Chemistry and Physics</u> 126 - 3 (2011) 711-716</p> <p>9) Enhanced optical modulation due to SPR in gold nanoparticles embedded WO₃ thin films <u>Journal of Alloys and Compounds</u> 509 – 5 (2011) 1729 -1733</p> <p>10) Chemical functionalization of carbon nano tube <u>PROCEEDING OF INTERNATIONAL CONFERENCE ON RECENT TRENDS IN APPLIED PHYSICS - (2013)</u></p>
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Dr. H. P. Deshmukh
Principal Investigator



Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

MAJOR RESEARCH PROJECT

Title : Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells

PRINCIPAL INVESTIGATOR : DR. H. P. DESHMUKH

F. No. 40-466/2011 (SR), dated: 19th October 2012

F. No. 40-466/2011 (SR), dated: 30th June 2011

Report of period : 1st July 2012 to 30th June 2015

HEAD WISE DETAILS OF ACCOUNTS

1. BOOKS & JOURNALS

Sr. No.	Items	Amount Approved	Grant released as 1 st installment	Amount spend
1.	Books & Journals	Nil	Nil	Nil

2. EQUIPMENTS

Sr. No.	Date	Description	Quantity	Agency	Amount
1.	28/12/2011	S.S. 316 Autoclave (25 ml)	01	Alpro Equipments	7500
				+Vat 12.5%	938
				Total	8438
2.	24/04/2013	Vertical Autoclave (35 Lit.)	01	VHS	63900
		Digital Muffle Furnace	01	VHS	63900
				Total	127800
				+Vat 12.5%	15975
				Total	143775
3.	28/06/2013	Kaspersky Antivirus CD	02	World Tele-communication	1560
4.	20/08/2013	S.S. 316 Autoclave (100 ml)	01	Alpro Equipments	9500
				+Vat 12.5%	1188
				Total	10688
5.	21/09/2013	Sensor (Ceramic)	01	Sharad Agency	275
				+Vat 12.5%	34
				Total	309
6.	03/12/2013	pH Meter Tester	01	Sharad Agency	5470
				+Vat 12.5%	684
				Total	6154

7.	26/08/2014	Shimatzu Digital Balance	01	VHS	41310
				+Vat 12.5%	5164
				Total	46474
8.	29/12/2014	Teflon liner (100 ml)	01	Alpro Equipments	7500
				+Vat 12.5%	938
				Total	8438
9.	29/06/2015	Pendrive 32 GB	02	World Tele-commu.	2000
Grand Total of Equipments					227836

3. HONORARIUM TO PROJECT FELLOW @ 8000/-p.m.

Sr. No.	Name of P.F.	Month	Amount
1.	Miss Bhosale Varada Dattatray	October 2011	5419
2.	Miss Bhosale Varada Dattatray	November 2011	8000
3.	Miss Bhosale Varada Dattatray	December 2011	8000
4.	Miss Bhosale Varada Dattatray	January 2012	8000
5.	Miss Shaikh Anjum Akbar	February 2012	3586
6.	Miss Shaikh Anjum Akbar	March 2012	8000
7.	Miss Shaikh Anjum Akbar	April 2012	8000
8.	Miss Shaikh Anjum Akbar	May 2012	8000
9.	Miss Shaikh Anjum Akbar	June 2012	8000
10.	Miss Shaikh Anjum Akbar	July 2012	8000
11.	Miss Shaikh Anjum Akbar	August 2012	8000
12.	Miss Shaikh Anjum Akbar	September 2012	8000
13.	Miss Shaikh Anjum Akbar	October 2012	8000
14.	Miss Shaikh Anjum Akbar	November 2012	8000
15.	Miss Shaikh Anjum Akbar	December 2012	8000
16.	Miss Shaikh Anjum Akbar	January 2013	8000
17.	Miss Shaikh Anjum Akbar	February 2013	6857
18.	Miss Shaikh Anjum Akbar	March 2013	8000
19.	Miss Shaikh Anjum Akbar	April 2013	8000
20.	Miss Shaikh Anjum Akbar	May 2013	5419
21.	Mr. Vavale Sudhir Dnyaneshwar	July 2013	7742
22.	Mr. Vavale Sudhir Dnyaneshwar	August 2013	8000
23.	Mr. Vavale Sudhir Dnyaneshwar	September 2013	8000
24.	Mr. Vavale Sudhir Dnyaneshwar	October 2013	8000
25.	Mr. Vavale Sudhir Dnyaneshwar	November 2013	8000
26.	Mr. Vavale Sudhir Dnyaneshwar	December 2013	8000
27.	Mr. Vavale Sudhir Dnyaneshwar	January 2014	8000
28.	Mr. Vavale Sudhir Dnyaneshwar	February 2014	8000
29.	Mr. Vavale Sudhir Dnyaneshwar	March 2014	8000

30.	Mr. Vavale Sudhir Dnyaneshwar	April 2014	8000
31.	Mr. Vavale Sudhir Dnyaneshwar	May 2014	8000
32.	Mr. Vavale Sudhir Dnyaneshwar	June 2014	8000
33.	Mr. Vavale Sudhir Dnyaneshwar	July 2014	8000
34.	Mr. Vavale Sudhir Dnyaneshwar	August 2014	8000
35.	Mr. Vavale Sudhir Dnyaneshwar	September 2014	8000
36.	Mr. Vavale Sudhir Dnyaneshwar	October 2014	8000
37.	Mr. Vavale Sudhir Dnyaneshwar	November 2014	8000
38.	Mr. Vavale Sudhir Dnyaneshwar	December 2014	8000
Grand Total of Fellowship of Project Fellow			293023

4. CHEMICAL/GLASSWARE/CONSUMABLE

Sr. No.	Date	Description	Quantity	Agency	Amount	
1.	02/02/2012	Titanus Chloride	500 ml	Yash Enterprises	1190	
				+Vat 5%	60	
				Total	1250	
2.	10/02/2012	Titanylacetylacetonate Merc (made in Germany)	25 mg	VHS	6250	
				+Vat 12.5%	781	
				Total	7031	
3.	01/09/2013	Titanylacetylacetonate Merc (made in Germany)	50 mg	VHS	12500	
				+Vat 12.5%	1563	
				Total	14063	
4.	14/10/2013	Hydrochloric Acid (AR grade)	500 ml	Sharad Agency	207	
		Nitric Acid (AR grade)	500 ml		216	
		NaCl (Extra pure)	500 gm		130	
		Titanium trichloride TiCl ₃	250 ml		1305	
		Titanium Tetraisopropoxide	250 ml		1215	
		Tri-ethanolamine AR grade	500 ml		486	
		Toluene AR grade	500 ml		283	
		Glass Beaker 100 ml (Borosil)	6 no.		313	
		Glass Beaker 25 ml (Borosil)	6 no.		366	
		Hand Gloves	6 no		351	
		Eonpipette variable volume (100 to 1000 µl)	1 no.		3599	
					Total	8471
					+Vat 12.5% or Vat 5 %	771
				Total	9232	

5.	03-03-2014	Fluorine doped tin oxide slides (Pack of 5 Slides)	1 Pack	Sharad Agency	6602
		Titanium(IV) butoxide	250 ml		5182
		HCl (AR grade)	1 litre		414
		Cadmium nitrate AR grade	100 gm		347
		Cadmium chloride monohydrate	100 gm		720
		Sodium sulphide	500 gm		216
		Sodium sulphite anhydrous	500 gm		201
		Selenium (metal) powder	250 gm		7002
		Methanol AR grade	5 litre		1710
		Cadmium acetate dihydrate AR	100 gm		414
		Ethanol [China]	2 litre		648
		Laboline (Thomaklin)	1 litre		342
		Glass Slide Box (50 Nos.)	2 No.		126
		Tissue Paper Roll	2 No.		86
		Acetone AR grade	1 litre		558
		Thiourea AR grade	500 gm		585
				Total	25173
				+Vat 5 %	1216
				+Vat 12.5 %	26
				+Vat 20 %	130
				Total	26545
6.	03/03/2014	Dye N-719	1 gm	Sharad Agency	42880
				+Vat 5 %	2144
				Total	45024
7.	26/08/2014	Titanium(IV) butoxide	250 gm	VHS	5182
		Selenium (metal) powder	250 gm		6975
		Titanium trichloride TiCl ₃	500 ml		2610
		Titanium Tetra-isopropoxide	500 ml		2430
		Titanylacetylacetonate (Merc)	50 gm		13500
				Total	30697
				+Vat 12.5 %	3837
				Total	34534
8.	08/05/2015	Iodolyte AN-50	20 ml	Vijay Chemicals	10110
		Platisol T	5 ml		3620
		Meltonix 1170-25, 30X20 cm	1 Pc		4977
		Ti-Nanoxide T/Sp	10 gm		12975
				Total	31682
				+Vat 12.5 %	3960
				Total	35642
9.	20/02/2015	Titanylacetylacetonate Merc (made in Germany)	50 mg	VHS	13500
				+Vat 12.5%	1688
				Total	15188

10.	25/06/2015	Titanylacetylacetonate Merc (made in Germany)	50 mg	VHS	13500
				+Vat 12.5%	1688
				Total	15188
Grand Total of Chemical/Glassware/Consumable					203697

5. HIRING SERVICES

Sr. No.	Items	Amount Approved	Grant released as 1 st installment	Amount spend
1	Hiring Services	Nil	Nil	Nil

6. CONTINGENCY

Sr. No.	Date	Description	Amount
1.	10-02-2012	Tata photon +	5000
2.	19-01-2013	Tata photon +	5000
3.	16-07-2013	Tata photon +	5000
4.	15-04-2014	Internet Charges	1310
5.	15-05-2014	Tata photon +	5000
6.	09-06-2014	Xerox	438
7.	02-07-2014	Laser Print	1628
8.	04-09-2014	XRD Charges	1000
9.	10-10-2014	Laser Print	1124
10.	15-10-2014	Xerox	1062
11.	16-10-2014	Internet Charges	1310
12.	09-11-2014	Paper A4 Size	180
13.	14-11-2014	XRD Charges	1000
14.	14-11-2014	Internet Charges	1310
15.	28-11-2014	Laser print & Binding	742
16.	02-12-2014	Laser Print	1628
17.	04-12-2014	XRD Charges	600
18.	04-12-2014	Laser print	976
19.	04-12-2014	XRD Charges	1700
20.	05-12-2014	Xerox	795
21.	10-12-2014	Internet Charges	1310
22.	21-12-2014	Internet Charges	996
23.	02-01-2015	Internet Charges	1310
24.	21-01-2015	Laser Print	646
25.	25-01-2015	Internet Charges	1965
26.	30-01-2015	XRD Charges	1000
27.	12-02-2015	Flex Poster (for Conference) Charges	280
28.	20-02-2015	XRD Charges	800

29.	21-02-2015	Internet Charges	1965
30.	11-03-2015	FESEM and EDAX Charges	3100
31.	21-03-2015	Internet Charges	1965
32.	15-04-2015	Internet Charges	1965
33.	28-05-2015	Internet Charges	1965
34.	26-06-2015	Tata photon +	5000
35.	26-06-2015	XRD Charges	600
36.	29-06-2015	XRD Charges	1000
37.	29-06-2015	FE-SEM Charges	3800
38.	29-07-2015	Registration charges for Paper presentation in International Conference	3000
Total of Contingency			69470

7. TRAVEL / FIELD WORK

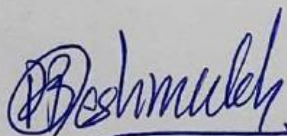
Sr. No.	Date	Perticular	Amount
1.	16/01/2012 to 19/01/2012	Visit to Shivaji University, Kolhapur for Reference work	4028
2.	06/02/2012 to 08/02/2012	Visit of Project Fellow to Shivaji University, Kolhapur	536
3.	24/05/2013 to 25/05/2013	Visit to Shivaji University, Kolhapur for Reference work	4460
4.	01/07/2013	Honorarium and T.A. for the subject expert called for interview of P.F. (Rs 500 + Rs 180)	680
5.	12/01/2014 to 15/01/2014	Visit to Shivaji University, Kolhapur for characterization of samples of the thin films like XRD, SEM etc.	5182
6.	07/02/2014 to 09/02/2014	Mid-term presentation at Delhi	9985
7.	04-09-2014	Riksha charges for analyzing XRD	152
8.	29-10-2014	Riksha charges for analyzing XRD	154
9.	14-11-2014	Riksha charges for analyzing XRD	158
10.	28-11-2014	Riksha charges for analyzing XRD	158
11.	04-12-2014	Riksha charges for analyzing XRD	158
12.	25-12-2014	Riksha charges for analyzing SEM	160
13.	04-12-2014	Riksha charges for analyzing SEM	156
14.	22-12-2014	Riksha charges for analyzing SEM	162
15.	14-12-2014	Riksha charges for analyzing SEM	158
16.	21-01-2015	Visit to Solapur University, Solapur for references, XRD and discussion etc.	6315

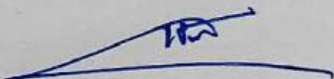
17.	23-01-2015	Riksha charges for analyzing XRD	160
18.	30-01-2015	Riksha charges for analyzing XRD	162
19.	11-02-2015	Riksha charges for analyzing XRD	160
20.	20-02-2015	Riksha charges for analyzing XRD	156
21.	02-03-2015	Riksha charges for FE-SEM & EDAX	160
22.	11-03-2015	Riksha charges for FE-SEM & EDAX	162
23.	22-06-2015	Visit to Shivaji University, Kolhapur for characterization of samples of the thin films like XRD, SEM etc.	7605
24.	20-06-2015	Kolhapur Toll	20
25.	22-06-2015	Kolhapur Toll	20
Grand Total of TRAVEL / FIELD WORK			41207

8 OVERHEAD CHARGES


1.	20-06-2015	Overhead charges	Y. M. College, Pune	52800
	TOTAL (1+2+3+4+5+6+7+8)			8,88,033

(In words - Rs. Eight lakh eighty eight thousand thirty three only)


Dr. H. P. Deshmukh
Principal Investigator


Dr. K. D. Jadhav
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.




M/S V.A. Dudhedia & Co
Chartered Accountant

VIJAYKUMAR A. DUDHEDIA
CHARTERED ACCOUNTANTS
M No 13989

Annexure-IX - 1

**PERFORMA FOR SUPPLYING THE INFORMATION IN
RESPECT OF THE STAFF APPOINTED UNDER THE
SCHEME OF MAJOR RESEARCH PROJECT**

UGC FILE NO. (1) F. No. 40-466/2011 (SR), dated: 19th October 2012

(2) F. No. 40-466/2011 (SR), dated: 30th June 2011

Year of commencement :

11	10	2011
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TITLE OF THE PROJECT: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

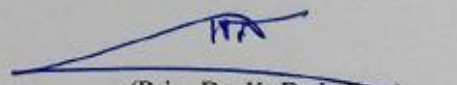
1.	Name of the Principal Investigator:	Dr. H. P. Deshmukh				
2.	Name of the University/College	Bharati Vidyapeeth Deemed University Yashwantrao Mohite College, Pune 38				
3.	Name of the Research Personnel appointed	Ms. Bhosale Varada Dattatray				
4.	Academic qualification	S.No.	Qualifications	Year	Marks	%age
		1.	M. Sc.	2011		63.9%
		2.	M.Phil	-	-	-
		3.	Ph.D.	-	-	-
5.	Date of joining Date of Resignation:	11/10/2011 09/02/2012				
6.	Date of Birth of Research Personnel	16/03/1986				
7.	Amount of HRA, if drawn	-				
8.	Number of Candidate applied for the post	2				

CERTIFICATE

This is to certify that all the rules and regulations of UGC Major Research Project outlined in the guidelines have been followed. Any lapse on the part of the University will liable to terminate the said UGC project.



(Dr. H. P. Deshmukh)
Principal Investigator



(Prin. Dr. K. D. Jadhav)
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

Annexure-IX - 2**PERFORMA FOR SUPPLYING THE INFORMATION IN
RESPECT OF THE STAFF APPOINTED UNDER THE
SCHEME OF MAJOR RESEARCH PROJECT****UGC FILE NO.** (1) F. No. 40-466/2011 (SR), dated: 19th October 2012(2) F. No. 40-466/2011 (SR), dated: 30th June 2011

Year of commencement :


11	10	2011
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TITLE OF THE PROJECT: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

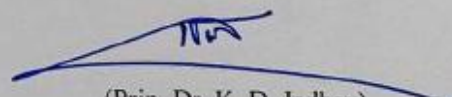
1.	Name of the Principal Investigator:	Dr. H. P. Deshmukh				
2.	Name of the University/College	Bharati Vidyapeeth Deemed University Yashwantrao Mohite College, Pune 38				
3.	Name of the Research Personnel appointed	Ms. Shaikh Anjum Akbar				
4.	Academic qualification	S.No.	Qualifications	Year	Marks	%age
		1.	M. Sc	2011		68.9%
		2.	M.Phil	-	-	-
		3.	Ph. D.	-	-	-
5.	Date of joining	17/02/2012				
	Date of Resignation:	31/05/2013				
6.	Date of Birth of Research Personnel	05/11/1988				
7.	Amount of HRA, if drawn	-				
8.	Number of Candidate applied for the post	2				

CERTIFICATE

This is to certify that all the rules and regulations of UGC Major Research Project outlined in the guidelines have been followed. Any lapse on the part of the University will liable to terminate the said UGC project.



(Dr. H. P. Deshmukh)
Principal Investigator



(Prin. Dr. K. D. Jadhav)
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

Annexure-IX - 3

**PERFORMA FOR SUPPLYING THE INFORMATION IN
RESPECT OF THE STAFF APPOINTED UNDER THE
SCHEME OF MAJOR RESEARCH PROJECT**

UGC FILE NO. (1) F. No. 40-466/2011 (SR), dated: 19th October 2012
(2) F. No. 40-466/2011 (SR), dated: 30th June 2011

Year of commencement :

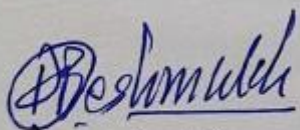
11	10	2011
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TITLE OF THE PROJECT: "Dual Sensitization of Hydrothermally grown TiO₂ for Efficient Solar Cells"

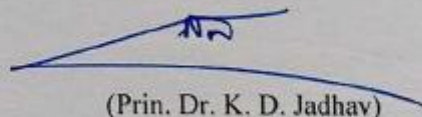
1.	Name of the Principal Investigator:	Dr. H. P. Deshmukh				
2.	Name of the University/College	Bharati Vidyapeeth Deemed University Yashwantrao Mohite College, Pune 38				
3.	Name of the Research Personnel appointed	Mr. Vavale Sudhir Dnyaneshwar				
4.	Academic qualification	S.No.	Qualifications	Year	Marks	%age
		1.	M. Sc.	2012		67.6%
		2.	M.Phil	-	-	-
		3.	Ph.D. Enrolled	2013	-	-
5.	Date of joining	02/07/2013				
6.	Date of Birth of Research Personnel	10/09/1989				
7.	Amount of HRA, if drawn	-				
8.	Number of Candidate applied for the post	1				

CERTIFICATE

This is to certify that all the rules and regulations of UGC Major Research Project outlined in the guidelines have been followed. Any lapse on the part of the University will liable to terminate the said UGC project.



(Dr. H. P. Deshmukh)
Principal Investigator



(Prin. Dr. K. D. Jadhav)
PRINCIPAL
YASHWANTRAO MOHITE COLLEGE
PUNE-38.

FINAL REPORT

MAJOR RESEARCH PROJECT ON

“Dual sensitization of hydrothermally grown TiO₂ for efficient solar cells”

OBJECTIVES:

The objectives of Major Research Project is the better understanding of some fundamental aspects of Dye sensitized solar cell as well as quantum dot sensitized solar cell. For this purpose, the behaviour of dye sensitized and quantum dot sensitized devices, photoanodes, photocathodes have been explored.

The main objectives of this project are:

- 1) To fine tune the process parameters to deposit good quality thin films of TiO₂ nanostructures by hydrothermal technique.
- 2) Optimization and development of Dye Sensitized Solar Cell (DSSC) with TiO₂ nanostructures and quantum dot solar cells.
- 3) Synthesis and characterization of the TiO₂ thin films deposited by hydrothermal method for structural, morphological, and optical properties like X-ray diffraction (XRD), energy dispersive X-ray microanalysis (EDX), Scanning electron microscopy (SEM) Field emission Scanning electron microscopy (FESEM) transmission electron microscopy (TEM), and UV-Visible spectrophotometer and FT-IR technique etc.
- 4) Optimization and development of CdS sensitized TiO₂ nanostructures for solar cells

- 5) Optimization and development of dye and CdS sensitized (dual sensitized) TiO₂ nanostructures for solar cells
- 6) To characterize the CdS-dye-TiO₂ thin films for structural, morphological, and optical properties like X-ray diffraction (XRD), energy dispersive X-ray microanalysis (EDX), Field emission Scanning electron microscopy (FESEM) and UV-Visible spectrophotometer and FT-IR technique.
- 7) To characterize thin films for their solar cells properties such as, current-voltage (I-V), Incident photo-to-current conversion efficiency (IPCE). The efficiency of prepared solar cells were estimated through I-V characterization measured with a Keithley 2400 source meter using an AM 1.5 (100 mW/cm²) solar simulator.
- 8) Fabrication of DSSCs based on these complementary combination and study of their performance
- 9) Sensitization of TiO₂ electrode with a Standard ruthenium-complex N719 dyes. Post treatment are carefully controlled and optimized.
- 10) Synthesis of the CdS Quantum Dots on oxide surface by Successive Ionic Layer Adsorption and Reaction (SILAR) Method.

SIGNIFICANCE OF THE STUDY

The topic is of current interest and related to the Energy Crisis, an alternate technology desperately needed for the country like India. Nowadays environmental pollution has increased extensively due to industrial as well as manmade activities. Complete removal of the pollutants for a clean and green environment is the centre point of attraction in today's scientific world.

The manufacturing cost of solar cell materials should be lower than that of materials deposited by vacuum deposition process. In the field of solar cells, one of the great strengths of TiO₂ is the ability to tailor the DSSC properties via modification of the structure. The solar cells technology is not new but the kind of work undertaken by us is

to fabricate low cost and stable TiO_2 films and their complementary CdS photovoltaic devices (solar cells). Secondly, the market penetration of these devices in India is very marginal due to their higher cost. Here our one of the objectives is to use cost-effective methods like hydrothermal technique to grow high quality complementary TiO_2 and CdS, CdS- TiO_2 thin films for solar cells device application.

The main points observed in this project are as follows

- 1) Metal oxides, such as titanium dioxide (TiO_2), have shown potential in solar cells.
- 2) During this research work several materials for solar cells sensitized TiO_2 were studied.
- 3) Each material has some advantages and disadvantages in very specific process.
- 4) Deposited CdS quantum dots on TiO_2 as a working electrode using the simple SILAR sensitization process.
- 5) Although the power conversion efficiency of nanoflowers and nanorods DSSC are not as good as compared to other inorganic 1st and 2nd generation solar cells, only low cost and abundantly available materials are needed for the DSSC and Quantum Dot Sensitised Solar Cells (QDSSC).
- 6) After TiCl_4 treatment on the TiO_2 film, the energy conversion efficiency enhances from 1.98% to 2.73% because TiCl_4 treatment improved the adhesion of the TiO_2 .
- 7) The bottle brush like dye sensitized rutile TiO_2 film has maximum photovoltaic performance. Hence the conversion efficiency of 6.63% has been achieved due to increased surface area which is much higher than nanorods or nanoflowers.

1. INTRODUCTION

In the modern world, energy has become one of the basic needs for life. With the increase in world population, energy demand is also rising. At present an average of 18 TW of energy rate was consumed by the world [1, 2]. The total demand of energy will increase to 28 TW in the year 2050 [3, 4]. Today, energy generation is mainly based on fossil resources [5]. More than 80% of energy is provided by fossil fuels (Oil, Natural gas, Coal etc.). Such fossil fuels are limited and the burning of fossil fuels creates lots of problems including green house gases (Carbon dioxide, water vapour, methane, nitrous oxide etc.). Hence there is global warming and harmful environmental pollutants (sulphur oxide, ash etc). These issues demand for a transition to alternative, renewable, environmental friendly and safer sources of energy. These include wind power, solar energy, hydropower, bio-energy and geothermal energy [6–8]. Solar energy is easily available all around the world. As compared to wind power and hydro energy, solar energy spreads out more evenly in the world. So that solar energy is the only alternative for fossil fuels and is available in tremendous amount all over the world. It is renewable and never goes to run out. The need for clean energy technologies has encouraged interest in new and efficient ways to capture and store sunlight [8-13]. There are several ways to capture solar energy to produce heat (solar thermal power), to convert directly into electricity by creating electron hole pairs in semiconductor photovoltaic [7]. Among new technologies, the photovoltaic energy conversion system is one of the most promising methods [15].

Researchers have developed a variety of different photo electrochemical cells that convert light to electricity. There are different varieties of solar cells commonly classified as three generation. First generation solar cells were silicon based which has high power conversion efficiency but they were so expensive [16]. The second generation photovoltaic material is based on the use of thin film solar cells. The efficiency of thin film solar cell is low as compared to silicon solar cells, but manufacturing cost is also low. Third-generation cells includes tandem solar cell, dye sensitized solar cell or Gratzel

solar cells [17] and Quantum dot sensitized solar cell [14, 15]. The most prominent is the dye sensitized solar cell, or DSSC. Now most efforts have focused on manufacturing of high efficiency DSSC.

Dye sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSSCs) are two promising alternative, cost-effective concepts for solar energy to electric energy conversion [10,15]. The configuration of a DSSC or a QDSSC consists of sintered TiO_2 films, ruthenium based dye or quantum dots (QDs) (i.e., sensitizers), and electrolytes. Upon the absorption of photons, the dyes or Quantum Dots generate excitons (i.e. electron hole pairs) [18].

1.1 DYE SENSITIZED SOLAR CELL (DSSC)

The process of dye sensitised solar cell is just like photosynthesis. In photosynthesis, light is converted into chemical energy. Chlorophyll and other pigments can eject electrons through photo-induced charge separation when struck by photons. The main component of a DSSC is a semiconducting material with a wide band gap. One such material is titanium dioxide (TiO_2). Dye sensitized solar cells (DSSCs) based on TiO_2 convert sunlight to electricity by using dye that was developed by O'Regan and Gratzel in 1991 [18]. DSSC based on ruthenium sensitizers have reached overall solar to electric power conversion efficiency (PCE) of 11.4% under standard air mass 1.5 G illumination [19-20]. DSSC materials are biocompatible and abundantly available. The technology can be expanded up to the terawatt scale without facing material supply problems. DSSCs are attractive, in part, because of a relatively high efficiency and low fabrication cost. The dye-sensitised solar cells (DSSC) also perform very well in sunny as well as cloudy days. They can be fabricated without the high vacuum, high energy and high temperature processes used in traditional silicon solar cell fabrication [18].

DSSCs can work even in low-light conditions. i.e. They can able to work under non-direct sunlight or cloudy skies, but the traditional designs suffer a "cut out" at some lower limit of illumination. So that the DSSCs can work for indoor use. They can collect the electrical energy from the lights in the house for small devices.

1.2 BASIC OPERATING PRINCIPLE

The Dye Sensitized Solar Cell (DSSC) uses the same basic principle as plant photosynthesis to generate electricity from sunlight [18]. The chlorophyll in green leaves generate electrons using the photon energy, which triggers the subsequent reactions to complete the photosynthesis process.

A typical DSSC is made of a layer of 10 to 15 μm thick oxide film sensitized by dye molecules. Dye molecules are the key component of a DSSC to have an increased efficiency through their abilities to absorb visible light photons [71]. Early DSSC designs involved transition metal coordinated compounds (e.g., ruthenium polypyridyl complexes) as sensitizers because of their strong visible absorption, long excitation lifetime and efficient metal to ligand charge transfer [18]. The primary dye TiO_2 interactions are mediated by the dye adsorption mode on the semiconductor surface. A crucial characteristic for efficient dyes is the presence of suitable functional groups which can strongly bind to the surface of semiconducting metal oxides. This is fabricated on a glass substrate coated with a transparent conductive film which serves as photo anode and another conducting glass electrode platinum catalyst which serves as Counter electrode. The electrolyte is a key component in DSSC. Its function is to generate dye molecules at the photoelectrode. The electrolyte interacts with both TiO_2 nanomaterials and sensitizers [42]. Electrolyte solution contains I^-/I_3^- redox couples which are introduced into the space between the two electrodes as a conductive medium between the two electrodes [21]. The operating principle of DSC is summarized in fig. 1 [22].

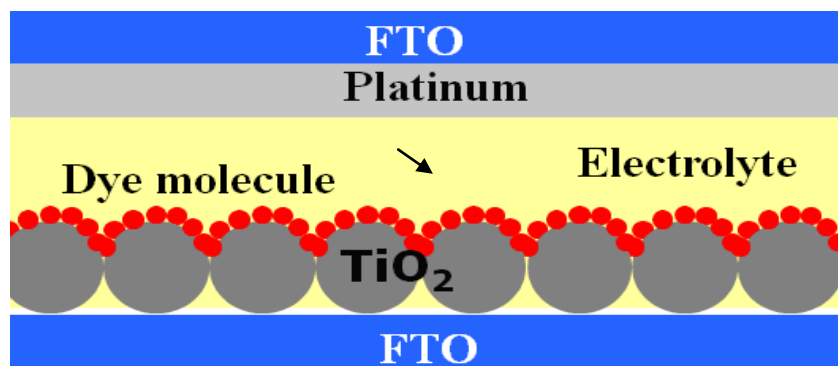
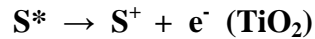


Figure 1 : Typical design of a dye-sensitized solar cell.

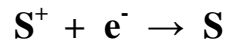
- 1) The light is absorbed by a sensitizer dye molecule and then it goes from the ground (S) to the excited state (S*).



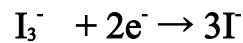
- 2) The sensitizing dye molecules are adsorbed on the surface of a wide band gap semiconductor typically TiO₂. After absorption of a photon, the dye gains the ability to transfer an electron to the conduction band of the semiconductor.



- 3) Injected electrons are transported between TiO₂ nanoparticles and counter electrode. The electron travels through the outer circuit performing work, reaches the back FTO electrode, and reduces the iodine in the electrolyte
- 4) The oxidized photo sensitizer (S⁺) accepts electrons from the (I⁻) ion redox mediator regenerating the ground state (S)



- 5) The oxidized redox mediator diffuses toward the counter electrode and is reduced to (I⁻) ions . The I⁻ is oxidized to the oxidized state, I₃⁻



Based on such a photovoltaic mechanism and to improve the conversion efficiency of a DSSC, one can either use dye molecules with a higher absorption coefficient and an extended long-wavelength absorption edge or increase the internal surface of the photoelectrode film for more dye adsorption to enhance optical absorption of the photoelectrode [23].

1.3 QUANTUM DOT SENSITIZED SOLAR CELL

First Reed et al. provided evidence of energy quantization in 1986 to describe the zero dimensional quantum boxes called quantum dot (QD) [30]. When the particle size is less than the exciton Bohr radius, quantum size effects typically occur [66]. Quantum dot

solar cells (QDSCs) have emerged as a viable alternative to other third generation solar cells such as dye sensitized [24, 25]. The quantum dot solar cell is one of the few solar technologies which promise to compete with fossil fuels but work is still needed to increase its performance. Recently nanotechnology have opened up new approach for harvesting light energy that extends towards the visible and the infrared (IR) region of the solar spectrum using semiconductor quantum dots (QDs) with tunable band edges [10, 26-28]. QDs offer the advantageous features of photostability, size dependent optical properties and low costs. Thus, quantum dot sensitized solar cells (QDSSCs) have become one of the most popular subjects for research into the next generation of solar cells [26-28].

Quantum dot sensitized solar cell employs a narrow band gap which is able to absorb lower energy photons than the metal oxide layer. Semiconductors have properties that make them attractive over dyes. A dye is limited to a monolayer of coverage. This forces researchers to use exotic dyes with extremely high absorption cross sections leaving little room for improvement [29].

Quantum dot sensitized solar cell consist of working electrode with thin layer of wide band gap semiconductor (TiO_2) on conducting fluorine doped tin oxide glass surface and quantum dot sensitizer attached to its surface. This electrode dipped in polysulphide electrolyte solution.

The most commonly used and investigated QDs for QDSC are CdS and CdSe QDs. Due to their high quantum efficiency in the visible region, they have been sensitizing with TiO_2 films in an efficient way [31].

Quantum dot sensitizers can be synthesized by two fundamentally different techniques. Chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) are widely used methods for preparation of QDs on TiO_2 substrate.

1.4 PROPERTIES OF TITANIUM DIOXIDE (TiO_2)

Nowadays, many n-type semiconductors are studied and applied in several application fields, such as energy production, smart materials technology, chemical synthesis, whereas p-type semiconductors are rarely used because of their limited

presence in nature and usually too small band gap. As TiO_2 has various applications in field of electronics due to interesting properties like non-toxicity, stability in hydrogen plasma, good electrical, optical, piezoelectric nanorods, and moreover low price etc., they are attracted by the industrial community [72]. TiO_2 is a widely accepted superior semiconductor material for diverse applications due to its better physical and chemical properties. TiO_2 is the most commonly used semiconducting material in dye sensitized solar cells due to its low cost and high power conversion efficiency.

1.5 STRUCTURAL PROPERTIES

Three phases of Titanium Dioxide can be found in nature: (1) anatase tetragonal (2) brookite orthorhombic and (3) rutile tetragonal. Anatase and rutile are the most commonly observed phases among them. Rutile is the most stable form. Anatase and brookite both convert into rutile on heating [33].

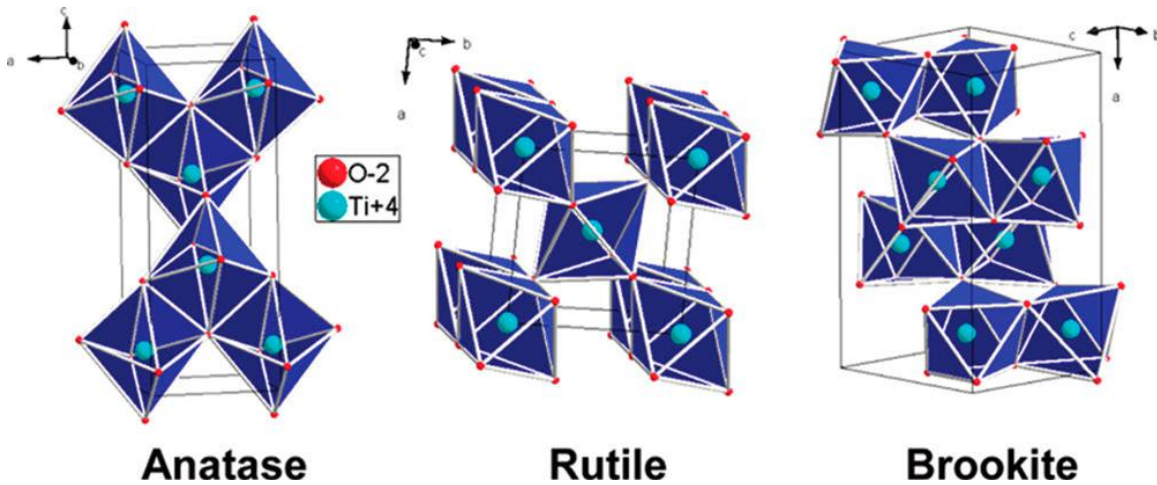


Figure 2 : Unit cells of TiO_2 polymorphs (a) Anatase, (b) Rutile and (c) Brookite

Titanium dioxide can exist in one of three bulk crystalline forms - rutile, anatase and brookite shown in figure 2 which can be described in terms of distorted TiO_6 octahedra with different symmetries or arrangements. The anatase structure consists of

edge-sharing TiO_6 octahedra, while the rutile and the Brookite frameworks exhibit both corner and edge-sharing configurations.

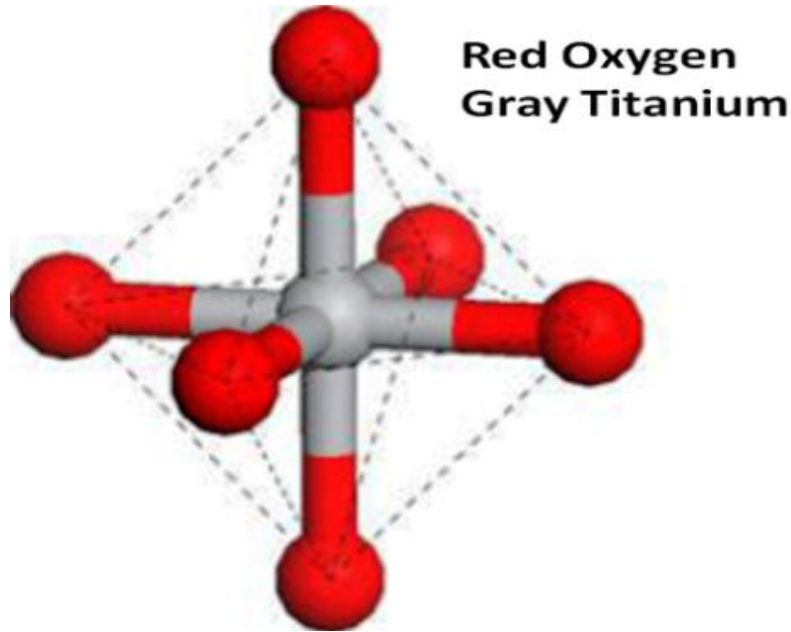


Figure 3 : Schematic representation of the distorted TiO_6 octahedron of TiO_2 .

Both anatase and rutile crystals are formed by chains of distorted TiO_6 octahedra (Figure 3) where each Ti atom is surrounded by 6 oxygen atoms. Each O atom is coordinated to three Ti atoms, lying in the same plane. Rutile phase is tetragonal with $a = 0.459 \text{ nm}$ and $c = 0.296 \text{ nm}$. Rutile is the most thermodynamically stable polymorph of TiO_2 at all temperatures, exhibiting lower total free energy than metastable phases of anatase and brookite [40]. The anatase phase is tetragonal but has a significantly longer c-axis (0.951 nm) compared to the a-axis (0.379 nm). The anatase structure is useful over other polymorphs for solar cell applications because of its potentially higher conduction band edge energy and lower recombination rate of electron hole pairs [41]. Brookite is orthorhombic and has a large unit cell. It is monoclinic with a particularly long a-axis (1.216 nm). However brookite phases are much less often observed in synthetic TiO_2 nanostructures [40].

1.6 APPLICATIONS OF TiO₂

Titanium dioxide used for the photoelectrode on account of its many advantages for photochemistry and photoelectron chemistry. It is a low cost, widely available, non-toxic and biocompatible material.

The polymorphic TiO₂ is extensively studied because of its specific properties and important roles in utilization of solar energy. TiO₂ has many applications in diverse areas like photo catalytic splitting of water (photocatalysis), photovoltaics, batteries, photonic crystals, UV blockers, smart coatings, and filling materials in textiles, paints, papers, cosmetics and biomedical sciences [33-36]. In 1972, Fujishima and Honda discovered the photocatalytic water-splitting on TiO₂ electrodes for hydrogen production [37], which is used for clean, low-cost and environmentally friendly production of hydrogen fuel from solar energy.

TiO₂ is one of the most widely used n-type large band gap semiconductor. Generally, the optical band gap (E_g) of TiO₂ varies with its structure [36] and for crystalline anatase and rutile being 3.2 eV and 3.0 eV [35], respectively. As rutile can absorb light of a wider wavelength range, it would be assumed that the photocatalytic performance of rutile would be superior to that of anatase [38].

Nanostructure TiO₂ with various morphologies has been synthesized, such as nanoparticles, nanorods and nanotubes. These nanostructures simultaneously offer a large surface area for uniform deposition of dye and quantum dots. Excellent light trapping characteristics, lower charge carrier recombination rates, and a highly conductive pathway for charge carrier collection, resulting in a highly efficient photoanode for solar cell applications [39].

Hence, it is very important to synthesize the TiO₂ nanoparticles with desired crystal structures and controlled particle size. Several methods have been used for synthesis of TiO₂ nanostructures for photo electrochemical and dye sensitized solar cell applications [15]. It would be an added advantage if the required TiO₂ nanoparticles are synthesized at low temperatures. The deposition of TiO₂ thin films, on various substrates was achieved by various methods such as chemical vapour deposition. Successive ionic layer adsorption and reaction (SILAR) [49]. Spray Pyrolysis [51] hydrothermal [53], DC

magnetron sputtering [50], Chemical bath deposition [52], pulsed laser deposition [54] and sol–gel method [15]. Hydrothermal synthesis is highly recommended to be developed to produce TiO_2 thin films of high quality for DSSCs in comparison with other method. This method is simple and has low manufacturing cost. The features of the hydrothermal method include excellent control over the deposition process, low cost and large scale deposition capability on various types of substrates. Recently, single crystalline TiO_2 nanorods and microspheres with a rutile phase have been successfully grown on the top of fluorine-doped tin oxide (FTO) coated glass, by a hydrothermal method [50].

1.7 CADMIUM SULPHIDE

Cadmium sulphide (CdS) is a II-VI semiconductor compound with a direct band gap of around 2.42 eV for a bulk material. It can attain three types of crystal structures namely wurtzite, zinc blend and high pressure rocksalt phase as shown in figure 4.

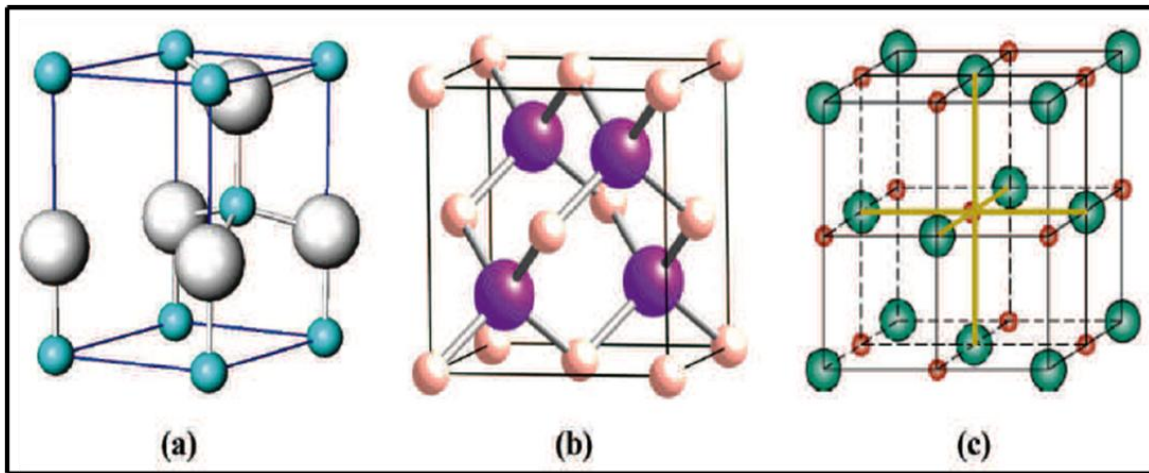


Figure 4 : A representative diagram of unit cell for crystal structure of CdS , showing (a) wurtzite (b) zinc blend and (c) rock salt phases.

Among these, wurtzite is the most stable structure and is easy to synthesize [43]. Wurtzite phase have been observed in both the bulk and nanocrystalline CdS while cubic and rock-salt phases are observed only in nanocrystalline CdS [65]. In hexagonal wurtzite and cubic zinc blend, each atom is coordinated to four other atoms in tetrahedral fashion such that each atom has four neighbouring atoms of the opposite type. It exhibits intrinsic n-type of conductivity caused by sulphur vacancies due to excess cadmium atoms.

Due to its unique optical, electronic and magnetic properties; CdS has been extensively investigated in applications such as photovoltaic devices [57-59] light emitting diodes [60-61], photocatalysis and high efficiency transistors [62]. Particularly it has been found that when the particle size of CdS is smaller than or comparable to its exciton Bohr radius (5.8 nm) [63], then the band gap increases with decreasing particle size owing to quantum confinement effect. Nano-particles with such features are normally called as Quantum Dots (QDs). The unique property of QDs has made them very attractive for many applications including photovoltaic technologies. Among them, QD-sensitized solar cells have attracted much attention due to their potential for achieving panchromatic light absorption [59]. In this type of solar cells, inorganic semiconductor nanocrystals are used to replace conventional organic molecule based light absorber. However, one of the challenges for producing high performance CdS-sensitized solar cells is to incorporate CdS material onto TiO₂ film effectively and to achieve good interface contact at the CdS/TiO₂ hetero structure, which will ensure efficient electron separation and injection and a high CdS nanocrystals coverage, giving high light absorption.

• **LITERATURE SURVEY**

Internationally there are number of groups working on preparation of Dye sensitized solar cell and quantum dot solar cell. Over the last two decades the amount of research in the field of DSSC & QDSSC has increased exponentially. In this study, only literatures that are directly relevant to this project are included. However the work is mainly focused on the following aspects.

- **INTERNATIONAL STATUS**

The pioneer work of Michael Graetzel on dye sensitized solar cells of TiO_2 in 1991 attracted widespread attention of the scientists from all over the world [18]. There after rapid surge of research in this field caused in depth understanding of the related phenomena. Significant progress in this field took place, especially in the inorganic materials in thin film form. To cater the need of improved device performance many different aspects of modification of TiO_2 have been undertaken.

Aydil S. Et.al [50] reported a facile hydrothermal method to grow single crystalline rutile TiO_2 nanorods films on transparent conducting substrates. The synthesis procedure was conducted at 150°C and reaction time was 18 hour. He observed 3% light to electricity conversion efficiency by employing $4\mu\text{m}$ long TiO_2 nanorod film as a photoanode in DSSC.

Xing zhong zhao et. al. [14] Synthesized anatase TiO_2 sols via hydrothermal reaction using tetra butyl titanate as the starting material. As synthesized sols were used in fabrication of DSSC. He observed that dispersion state of particles in sols was changed with temperature. He achieved best photovoltaic performance due to the improved dispersion of nanocrystallites in the sols.

Michael Graetzel et.al. [11] Demonstrate novel architecture for the DSSC photoanode which consist of hierarchical assemblies of nanocrystalline particles of anatase TiO_2 , morphologically resembling a tree, giving rise to a forest like structure. The trees orderly grown on TiO_2 coated FTO by a careful control of the Pulsed Laser deposition (PLD) method. They achieved 5 % light to electricity conversion efficiency for films $7\mu\text{m}$ thick.

Xukai Xin et. al.[12] DSSCs were synthesized by capitalizing on a TiO_2 bi-layer structure composed of P-25 nanoparticle and freestanding anatase TiO_2 nanotube arrays as a photoanode by a two step electrochemical anodization. Prepared photoanode was treated with TiCl_4 and O_2 plasma exposure. They observed light to electricity conversion efficiency up to 8.02 %. Surface treatment of TiO_2 photoanode has been proven very beneficial in increasing dye loading and promising interaction between dyes and TiO_2 surface.

Xiong Y. et.al. [13] Highly ordered anatase 2D hexagonal mesoporous TiO_2 nanoparticles with a high surface area and large pore size were fabricated. They observed that the films became more porous, with a larger surface roughness, had higher surface areas and greater light scattering effects when meso TiO_2 was incorporated. The performance of these scattering layers in relatively large as compared to an equivalent cell prepared with P-25 films.

Lee et. al. [67] used alcohol as solvents in chemical bath deposition method to synthesized CdS quantum dots onto mesoporous TiO_2 films. They observed that due to alcohol, the system not only has a higher incorporated amount of CdS but also greatly inhibits recombination of injected electron. They obtained efficiency up to 1.84 %.

Kamat P.V. et.al.[68] reported Quantum Dot Sensitized Solar Cells with doping of CdS/CdSe films using Mn which enabled to achieve nearly 20% enhancement in the power conversion efficiency as compared to undoped films. The efficiency of 5.42% obtained with Mn-doped CdS/CdSe film which is one of the highest performing QDSSCs reported to date.

Sun L. et. al. [69] reported an efficient and noncorrosive polysulfide electrolyte for CdS Quantum Dot sensitized solar cells. With the use of this polysulfide electrolyte in organic solution, the performance of the cell showed an energy conversion efficiency of 3.2%.

Composites of TiO_2 with other in-organic materials proved to enhance power conversion efficiency. All DSSCs devices based on CdS, CdSe, thin films were developed to improve stability of the devices. CdS nanoparticles were used to protect the surface of TiO_2 thin films. It was found that the CdS nanoparticles could improve the solar cells performance of the TiO_2 films greatly. The experimental results indicates that the absorbance of the thin film was increased after the sensitization. [67, 68].

- **NATIONAL STATUS**

At the national level, there are very few groups working in the field of solar cells and to the best of our knowledge, no company, institute or laboratory is specifically working towards the fabrication of devices applications. However, research groups at

National Chemical Lab (NCL), Pune, Indian institute of Technology Bombay, Powai, Mumbai, Indian institute of Technology, Delhi, Defence Lab. Jodhpur, National Physical Lab (NPL), New Delhi and our group from Bharati Vidyapeeth, Pune are engaged in the development and characterization of solar cells. Though titanium oxide based DSSCs are being developed and studied by some of these groups; but the techniques used for deposition of these films by the said groups are magnetron sputtering, spray pyrolysis, electron beam evaporation and similar physical vapour deposition techniques. In India, there are no groups involved in the deposition of TiO_2 by simple hydrothermal method. We tried to fabricate the films by using hydrothermal method which are highly scalable, have high power conversion efficiency, low cost, good durability and stability.

To the best of our knowledge, solar cell devices are neither being produced nor being worked on in our country. So in continuation with the existing infrastructure and expertise, we would like to develop easily processable, efficient and stable devices based on TiO_2 thin films and to study their performance.

Ogale et. al. [71] from NCL Pune reported dye sensitized solar cells (DSSC) having thin anatase TiO_2 nanoleaves with high surface area. They observed that DSSCs made with nanoleaves show higher conversion efficiency (5.6%) than those made with nanoparticles (4.8%) and P-25 show conversion efficiency of 4.5% but the highest efficiency 6.5% was obtained for DSSCs by using 50:50 mixture of nanoleaves and nanoparticles.

Mali et. al. [50] reported a surfactant free synthesis of TiO_2 nanostructure by a simple and promising hydrothermal route. They synthesized different nanostructure like nanoparticle cluster, 1 D tetragonal nanorods, 3 D dendrites containing nanorods and 3 D hollow urchin like structure. These nanostructure possess effective high surface area for dye loading. They observed that the electrical conversion efficiency was up to 7.16 %.

Mane et. al. [70] synthesized nano structured rutile TiO_2 photoanode by simple wet chemical route at ambient temperature. After TiCl_4 surface post treatment they observed that there is increase in light to electricity conversion efficiency up to 4.4 %.

2. MATERIALS AND METHOD

2.1 METHODOLOGY

Good quality thin films of TiO_2 , CdS and CdS- TiO_2 will be synthesized. For the thin film deposition of TiO_2 the cost-effective and low temperature hydrothermal technique was used. The hydrothermal method is widely used for manufacturing small particles using aqueous or non aqueous solutions. The synthesis is typically implemented in autoclaves at elevated temperature and pressure. Different process parameters associated with both these techniques like film thickness, precursor concentration, deposition time and temperature etc. was carefully optimized.

The thin films of complimentary conducting polymer composites were characterized using Fourier transform infra-red spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDS), field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS) etc. techniques. Photovoltaic properties were studied by using current-voltage (I-V) characteristic method.

2.2 EXPERIMENTAL DETAILS

Materials and Chemicals

1. Fluorine doped Tin Oxide coated conducting glass electrodes, 3 mm thick, $7 \Omega\text{-cm}^{-2}$ Sigma-Aldrich
2. Titanium tetrachloride, Alfa Aesar
3. Titanium tetra isopropoxide (TTIP), Alfa Aesar
4. Titanium (IV) Butoxide (TBT), Alfa Aesar
5. Titanylacetylacetonate (merc made)
6. Hydrochloric acid from Thomas Baker
7. Ethanol
8. Methanol
9. Cadmium Nitrate

10. Cadmium Chloride
11. Copper Nitrate
12. Sodium sulphite
13. Selenium powder, Sigma-Aldrich
14. Sulfur powder
15. Potassium chloride
16. Ruthenium Dye N719, Sigma-Aldrich
17. Electrolyte: Iodolyte –AN 50, Solaronix Switzerland
18. Acetonitrile anhydrous 99.8%, Sigma-Aldrich
19. Platinum precursor solution: Platisol T, Solaronix Switzerland
20. Sealant: Meltonix 1170-60PF, Solaronix Switzerland
21. Nitric acid and sulfuric acid, Thomas Baker

3. PREPARATION OF TiO₂ THIN FILM

Many deposition parameters are involved in hydrothermal method and they are mutually dependent on each other. One of the parameters was varied and other parameters were kept constant.

The TiO₂ array was deposited on FTO film by using a hydrothermal method reported previously by Liu and Aydil [50]. In our experiment, tetra butyl titanate (C₁₆H₃₆O₄Ti) and hydrochloric acid (HCl, 38%) of analytical grade were used without further purification. Double distilled water was used throughout the preparation. The typical experimental procedures are depicted as follows: First 0.5 ml of tetra butyl titanate was added into mixture of the equal amount of double distilled water and concentrated hydrochloric acid. After stirring at ambient conditions for 0.5 hour, the solution became clear and transparent. Here the tetra butyl titanate was used as the precursor for the growth of TiO₂ arrays and the HCl was used to avoid the hydrolysis of the precursor. A FTO substrate was loaded in the autoclave with the conducting side facing up. The resulting solution was then transferred into a 100 ml Teflon-lined stainless steel autoclave and sealed properly. The hydrothermal reaction was conducted at 160⁰C for 8 hours. After the synthesis, the autoclave was cooled down naturally to room temperature. FTO substrate covered with TiO₂ was taken out, rinsed with deionized (DI) water and then dried in an electric oven. It was then annealed at 450 °C in air for 30 min.

The process parameters play a crucial role in determining the film properties in hydrothermal technique. In order to obtain desired film properties, optimum set of the process parameters is to be selected.

3.1 VARIATION IN DEPOSITION CONDITIONS OF TiO₂ FILMS.

The deposition of TiO₂ thin films on fluorine doped tin oxide (FTO) using a hydrothermal method reported previously by Liu and Aydil [50]. Optimization of various process parameters is done by the variation of one of the parameters. 160 ⁰C reaction temperature and 8 hours time for deposition were used as constant solution process parameters and amount of precursor was varied from 0.25 to 1 ml. Then these deposited

films were studied for their structural, morphological, and optical properties. The deposition conditions for the synthesis of TiO₂ films used in the present study are mentioned in table to obtain densely array of thin film.

3.1 Deposition conditions of solution for TiO₂ thin films

Solvent	Autoclave Temperature	Deposition Time	Amount of precursor
Water + HCl (1:1) volume ratio	160 °C	8 hours	0.25 - 1 ml

(A) X-RAY DIFFRACTION

The XRD investigations show that the TiO₂ samples deposited on FTO substrate. It is clear from the XRD patterns that all of the thin films consist of polycrystalline titanium dioxide with rutile crystal structure. Peak positions were indexed to (110), (101), (111), (210), (211), (002), (202) reflections and were common in all TiO₂ films, which supported well the formation of tetragonal rutile structure of TiO₂ films under the preparative conditions [JCPDS card no. 21-1276]. Some other additional peaks are due to FTO.

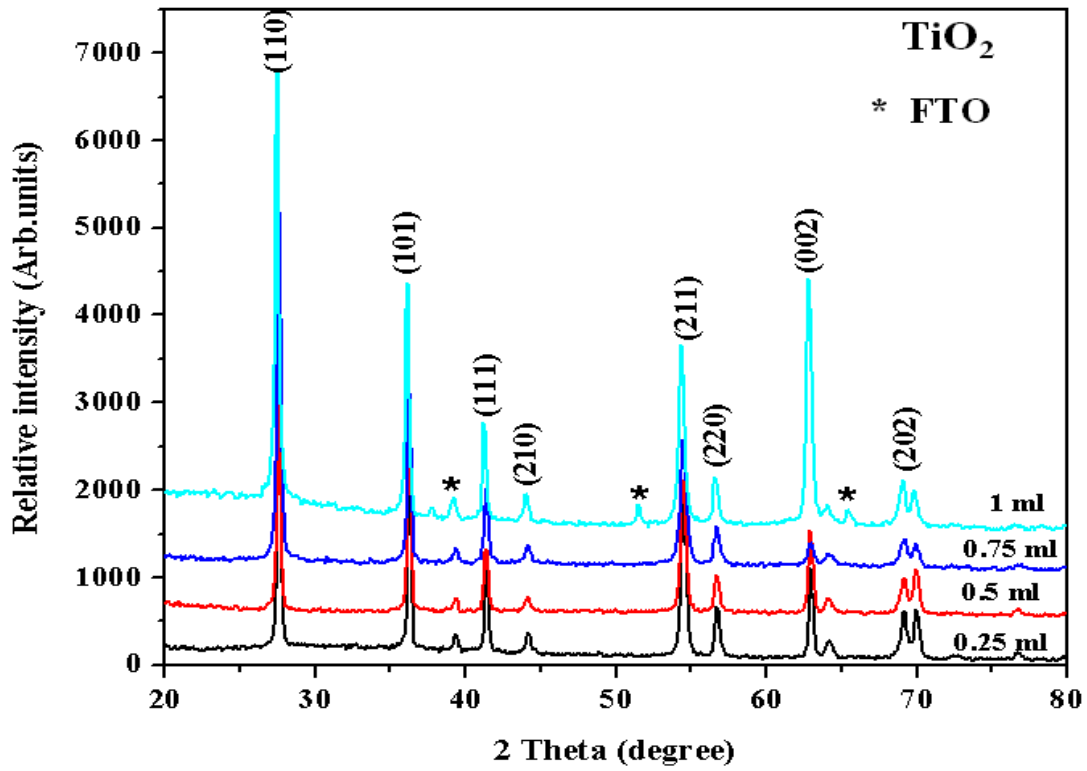


Figure 5 : XRD patterns of the TiO₂ films prepared by using a) 0.25 ml, (b) 0.5 ml, (c) 0.75 ml (d) 1 ml amount of titanium precursor.

We calculated the crystallite size using Scherrer's formula [64]

$$\text{Crystallite size} = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where λ is the wavelength, β is the full width at half maximum (FWHM) and θ is the diffraction angle. The crystallite size was increased with increase in precursor quantity up to 0.75 ml and again decreased appreciably. The TiO₂ films grown by using 0.75 ml precursor showed crystallite size of about 32 nm.

(B) SCANNING ELECTRON MICROSCOPY

Fig. 6 shows scanning electron microscopy (SEM) images of the TiO_2 films prepared at various amount of precursor. The effects of precursor variation by controlling the growth of TiO_2 nanostructure films on FTO substrates was optimized at amount of 0.75 ml precursor with reaction time 8 hours and temperature 160°C . At lower concentration of titanium butoxide, some defects in TiO_2 structures were observed. At 0.75 ml amount of precursor, there is increase in grain size with uniform distribution of the film.

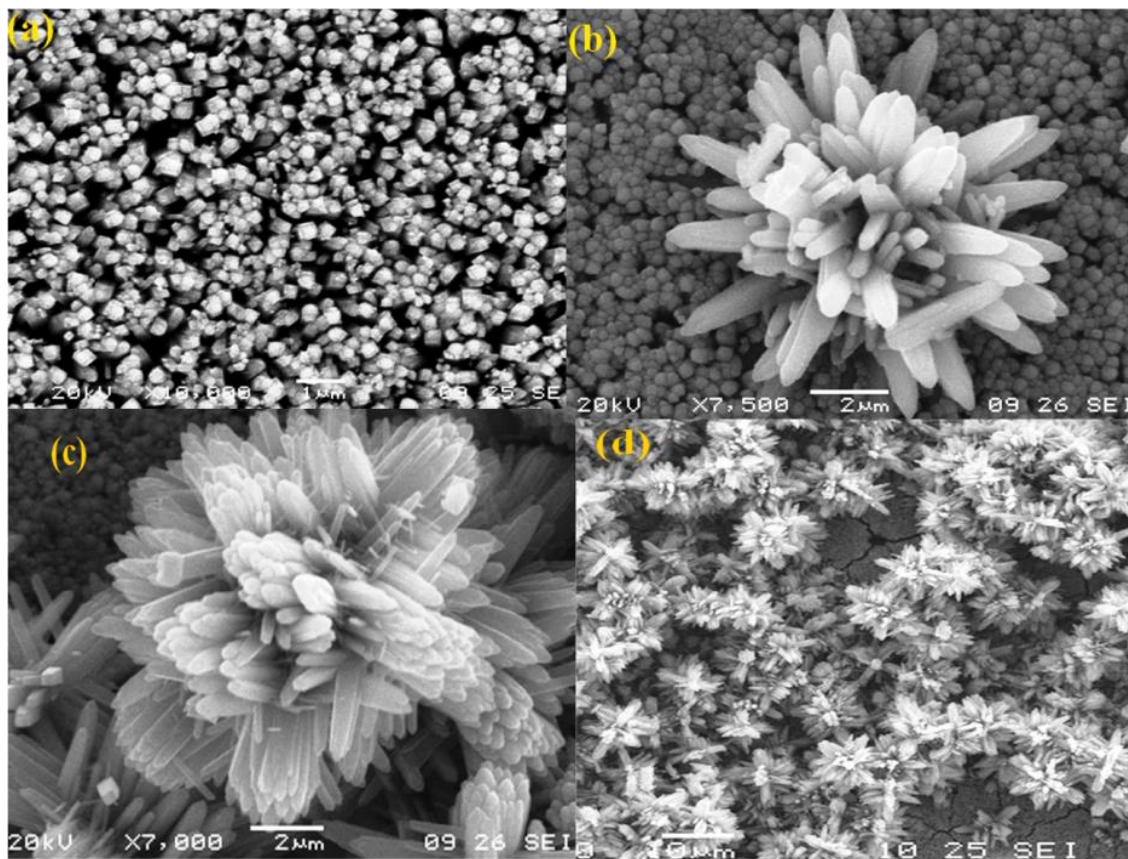


Figure 6 : SEM micrograph of TiO_2 films obtained by hydrothermal method with (a) 0.25 ml, (b) 0.5 ml, (c) 0.75 ml and (d) 1 ml amount of titanium precursor.

Further increases in concentration of precursor of 1 ml, the grains were dominant which eventually had decreased the uniformity of the film. Figure (6 c) indicates that every cluster consists of multiple nanorods with sharp sword ends and the nanorods cluster looks like the petal of nanoflowers. These nanoflowers with rod-petals could indicate the stability of nanoflowers. However, FTO was not covered entirely by TiO_2 nanoflower at lower amount of titanium precursor. The film revealed the formation of uniform morphology of the grains at 0.75 ml of titanium precursor. Therefore we kept this quantity constant throughout the experiments.

(C) OPTICAL ANALYSIS

The molar concentration effect on the TiO_2 films was investigated from UV-Vis analysis. The absorbance spectra of TiO_2 films is as shown in figure 7 (a).

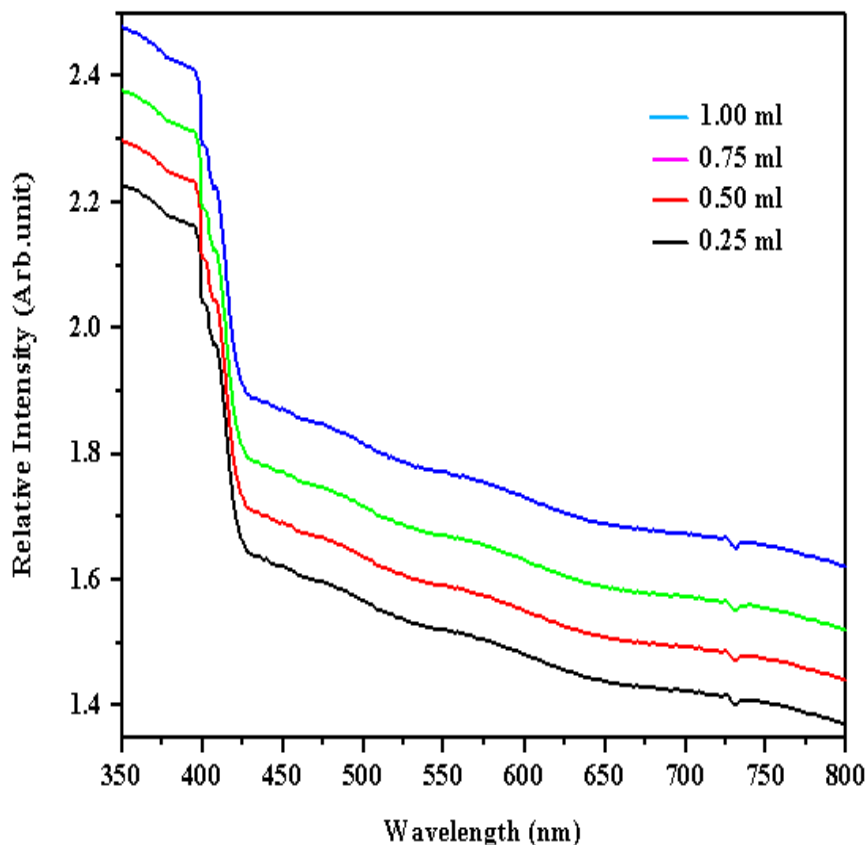


Figure 7 (a) : UV-Vis absorbance spectra of rutile TiO_2 for different amount of precursors.

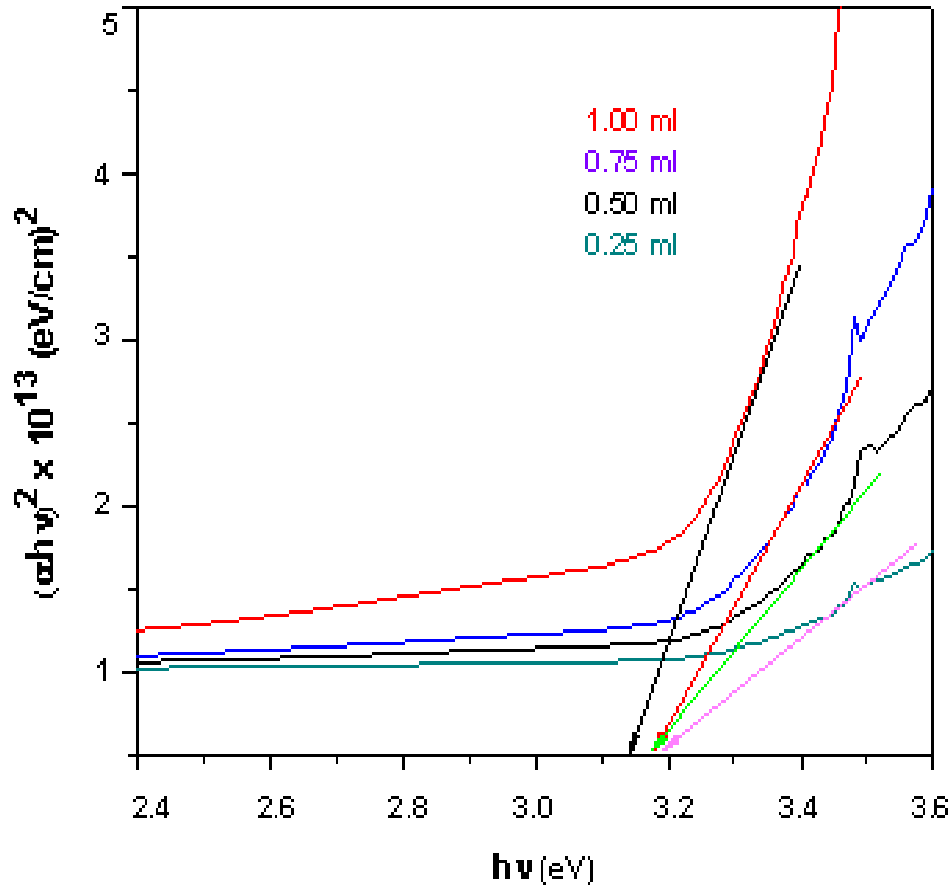


Figure 7 (b) : Band gap energy of rutile TiO₂ for different amount of precursors.

At low concentration of precursor, TiO₂ films absorb the visible light strongly through intermediate gap states created by the film defects such as oxygen vacancies and interstitial titanium atoms. These observations led us to conclude that the TiO₂ films formed at 0.75 ml concentration had fewer defects and intermediate products and consequently had better crystal quality.

The plot of $(\alpha h\nu)^2$ on the y-axis versus photon energy ($h\nu$) on the x-axis is as shown in figure 7 (b). Where $h\nu$ is the incident photon energy. The energy band gap was determined by extrapolating the linear part of $(\alpha h\nu)^2$ vs. ' $h\nu$ ' curve to $h\nu = 0$. The direct

band gap was changed with variation in molar concentration. Initially with increase in concentration from 0.25 ml to 0.75 ml the band gap was decreased from 3.2 eV to 3.15 eV. At 0.75 ml the band gap value obtained for TiO₂ film was 3.2 eV.

3.2 EFFECT OF REACTION TEMPERATURE

In the previous section, we have found that the required volume of precursor for the synthesis of TiO₂ film is 0.75 ml. In this set of experiment, we have varied the temperature parameter for developing uniform and densely TiO₂ thin films which are listed in the table.

Deposition conditions of solution for TiO₂ thin films

Precursor used	Solvent	Reaction Temperature	Quantity of Solution	Deposition Time
Tetra butyl titanate (C ₁₆ H ₃₆ O ₄ Ti)	Double distilled water and HCl (1:1 volume ratio)	120 °C -180 °C	60 ml	8 hours

(A) X-RAY DIFFRACTION

Fig. 8 shows the XRD pattern of TiO₂ at different reaction temperature. The XRD investigations show that the phase structure of rutile TiO₂ sample deposited on FTO substrate. It is clear from the XRD patterns that all of the thin films consist of polycrystalline titanium dioxide with rutile crystal. At lower temperature 120 °C samples obtained are poorly crystalline. After increasing reaction temperature sharp shape and narrow width of TiO₂ was obtained indicating that the TiO₂ material was highly crystalline. Upon treating titanium butoxide at 160 °C we got highly crystalline rutile phase. The Peak positions were indexed to (110), (101), (111), (211), (002), (301) reflections and were common in all TiO₂ films, which supported well the formation of tetragonal rutile structure of TiO₂ films under the preparative conditions. [JCPDS card no.21-1276].

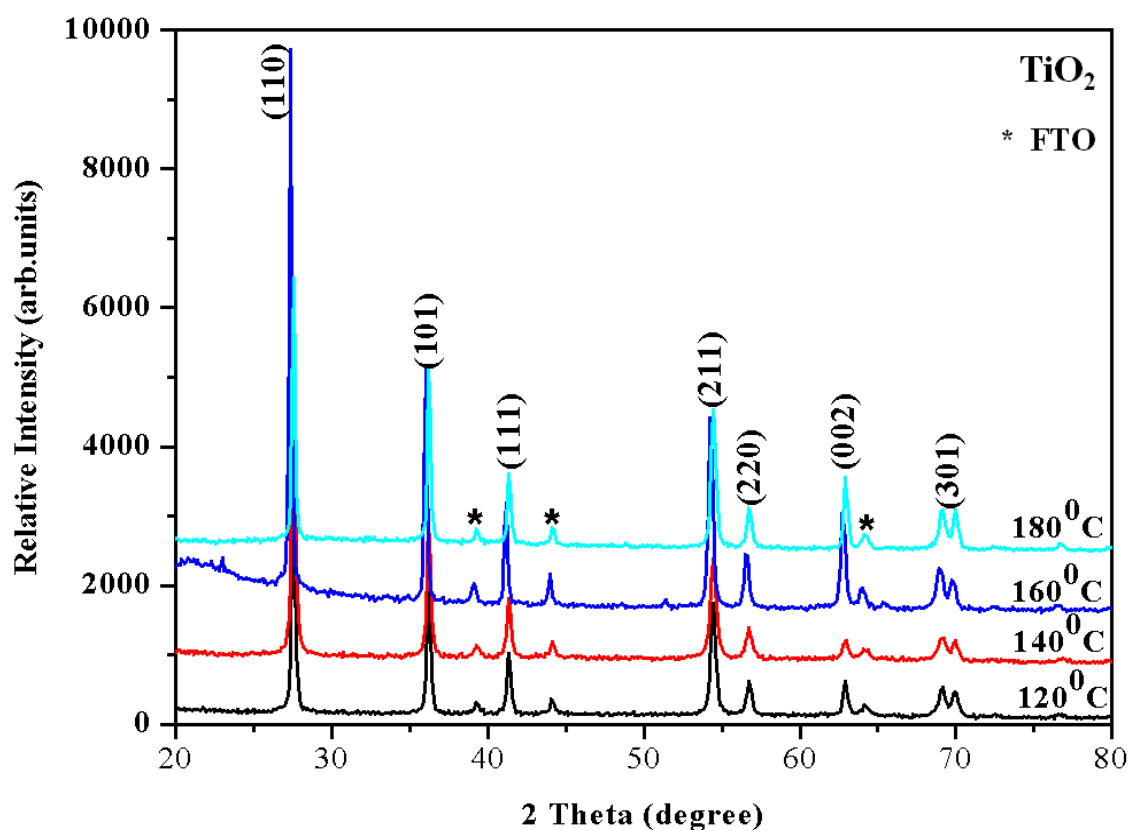


Figure 8 : XRD patterns of the TiO_2 films prepared at different reaction temperature.

The average crystallite size was estimated from the full width at half maximum (FWHM) data using Debye-Scherrer's formula. The average crystallite size for most intense peak (110) was found to be 35 nm.

(B) FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

Figure 9 shows typical FESEM images of TiO_2 nanostructures synthesized at different reaction temperatures. The reaction time was 8 hrs for each sample deposition. Fig 9 (a) shows that TiO_2 synthesized at 120°C on the FTO coated conducting substrate.

The compact TiO_2 clusters are deposited on entire surface of the FTO substrate. Fig 9 (b) shows that there are rapid changes in the surface morphology for the TiO_2 sample when deposited at temperature 140°C .

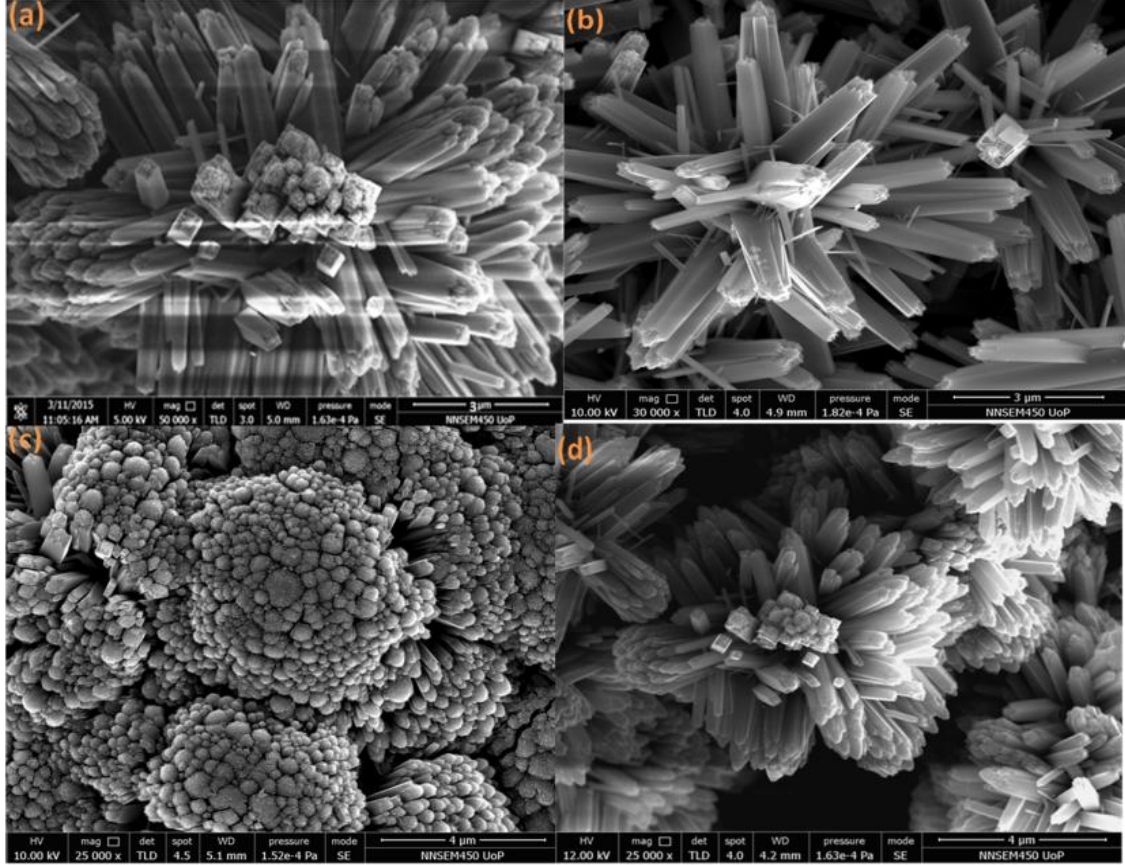


Figure.9 : FESEM micrograph of TiO_2 films obtained by hydrothermal method with reaction temperature (a) 120°C (b) 140°C (c) 160°C and (d) 180°C .

Therefore we have decided to increase the hydrothermal system temperature. figure 9 (c) shows that FESEM at 160°C uniform distribution of vertically aligned nanorods covered throughout the substrate. It shows novel nanoflowers like morphology having bunch of aligned nanorods. The diameter of such flower is about $3\ \mu\text{m}$. At 180°C , the sufficiently high temperature causes formation of 3D hollow urchin like morphology

due to higher surface energy. These results indicate that at higher temperatures the TiO_2 growth rate is too fast to allow it to be uniformly deposited on the template, resulting in a rougher surface morphology for the TiO_2 sample.

(C) OPTICAL PROPERTIES

The UV-Vis absorbance spectra of as-grown TiO_2 thin films in the wavelength range of 300–800 nm are as shown in figure 10 (a) in which the reaction temperature is varied from 120 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$.

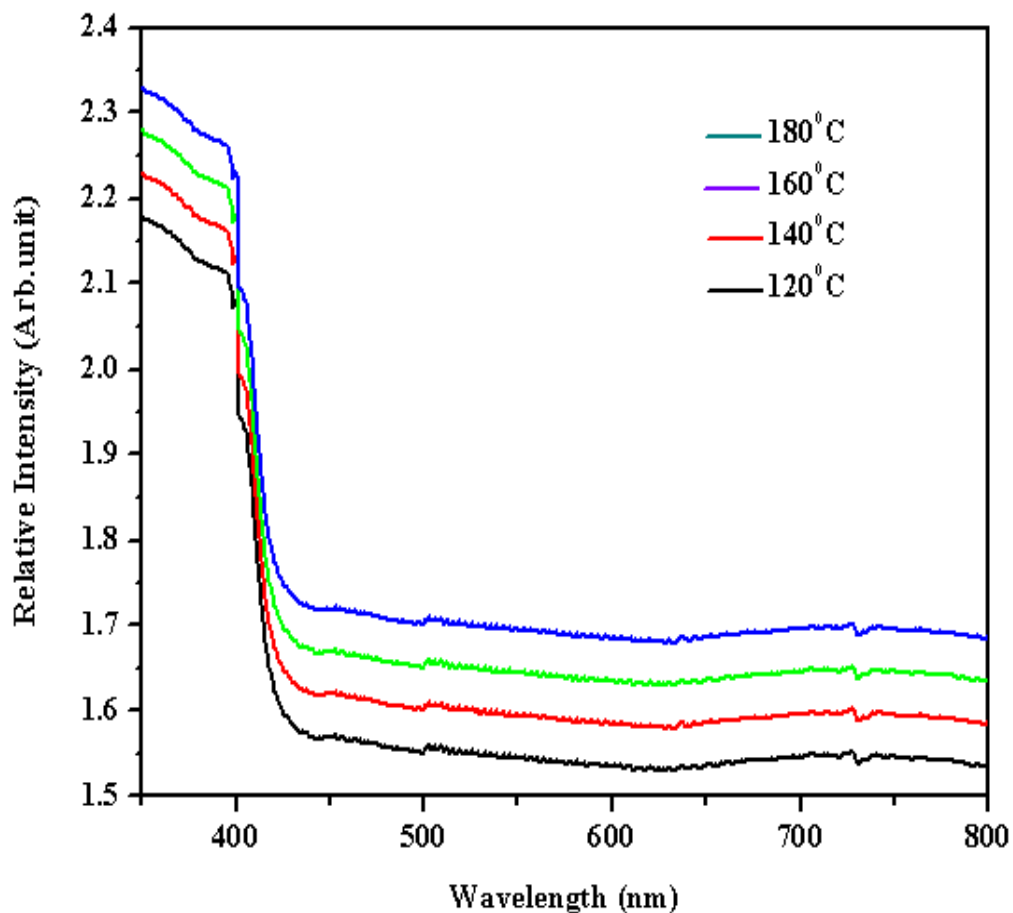


Figure 10 (a) : UV–Vis absorbance spectra of rutile TiO_2 for varying deposition temperature

The sharp absorption edge in absorption spectra shows that the deposited films are of high quality. The increase in absorbance may be due to increase in temperature of the reaction. The film deposited at low reaction temperature has very less absorbance peak. As the temperature increases from 120 °C to 180 °C, there was small change in absorbance spectra towards the visible region of the spectrum.

The absorption coefficient α calculated by applying the Tauc model [48], was used to evaluate the optical band gap of the TiO₂ thin film. Figure 10 (b) shows plots of $(\alpha h\nu)^2$ vs. $h\nu$ for the TiO₂ thin films deposited at different temperatures. As seen from figures, the values of optical band gaps of the films were increased from 3.11 eV to 3.19 eV as temperature was raised from 120 °C to 180 °C.

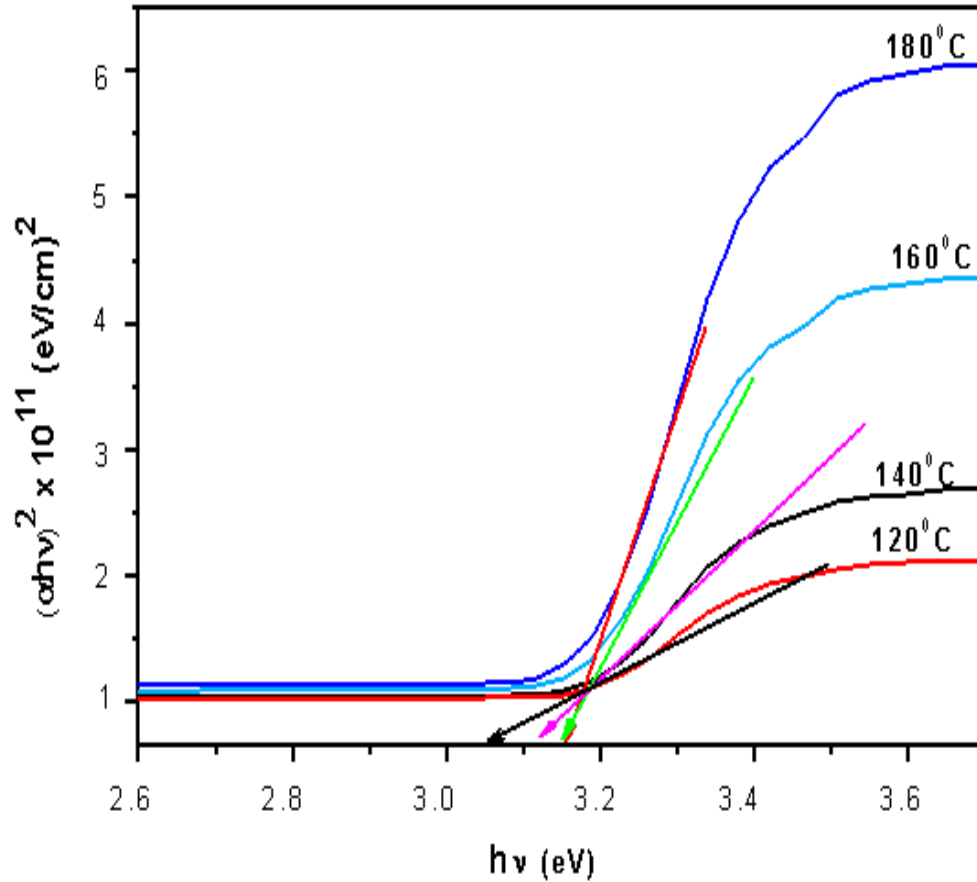


Figure 10 (b) : Band gap energy of rutile TiO₂ for varying deposition temperature.

3.3 EFFECT OF DEPOSITION TIME

In previous section, we have found that the required temperature of reaction for the synthesis of TiO_2 film is 160°C . In this set of experiment, we have varied deposition time and the other parameters are kept constant for developing uniform and densely aligned TiO_2 thin films as shown in the table.

Deposition conditions of solution for TiO_2 thin films

Precursor used	Solvent	Reaction Temperature	Quantity of Solution	Deposition Time
Tetra butyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$)	Double distilled water and HCl (1:1 volume ratio)	160°C	60 ml	4 -20 hours

(A) X-RAY DIFFRACTION

The XRD investigations show that the TiO_2 sample is deposited on FTO substrate. It is clear from the XRD patterns that all the thin films consist of polycrystalline titanium dioxide with rutile crystal structure [JCPDS card no. 21-1276] as shown in the figure 11. Peak positions were indexed to (110), (101), (111), (211), (002), (202) reflections and were common in all TiO_2 films

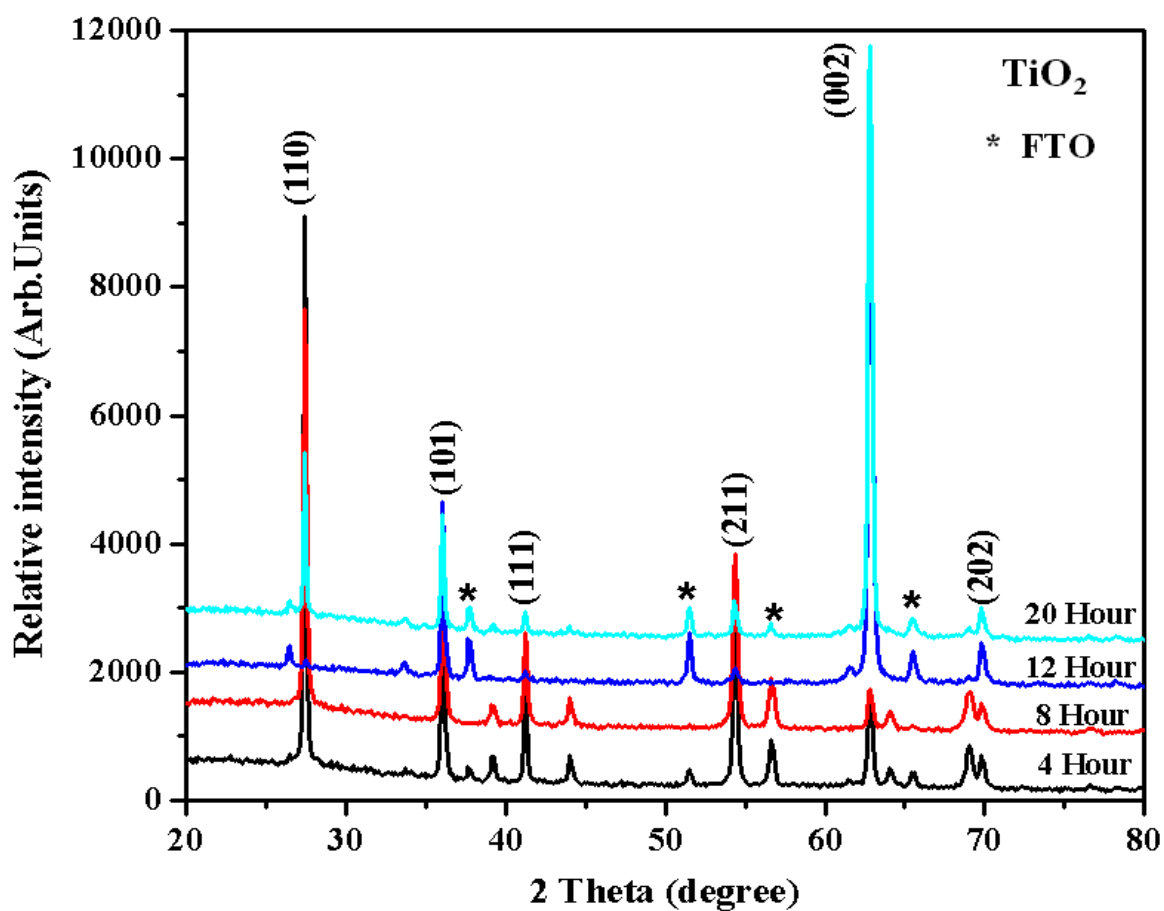


Figure 11 : XRD patterns of the TiO₂ thin films having deposition time (a) 4 hours ,
(b) 8 hours, (c) 12 hours and (d) 20 hours

(B) FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

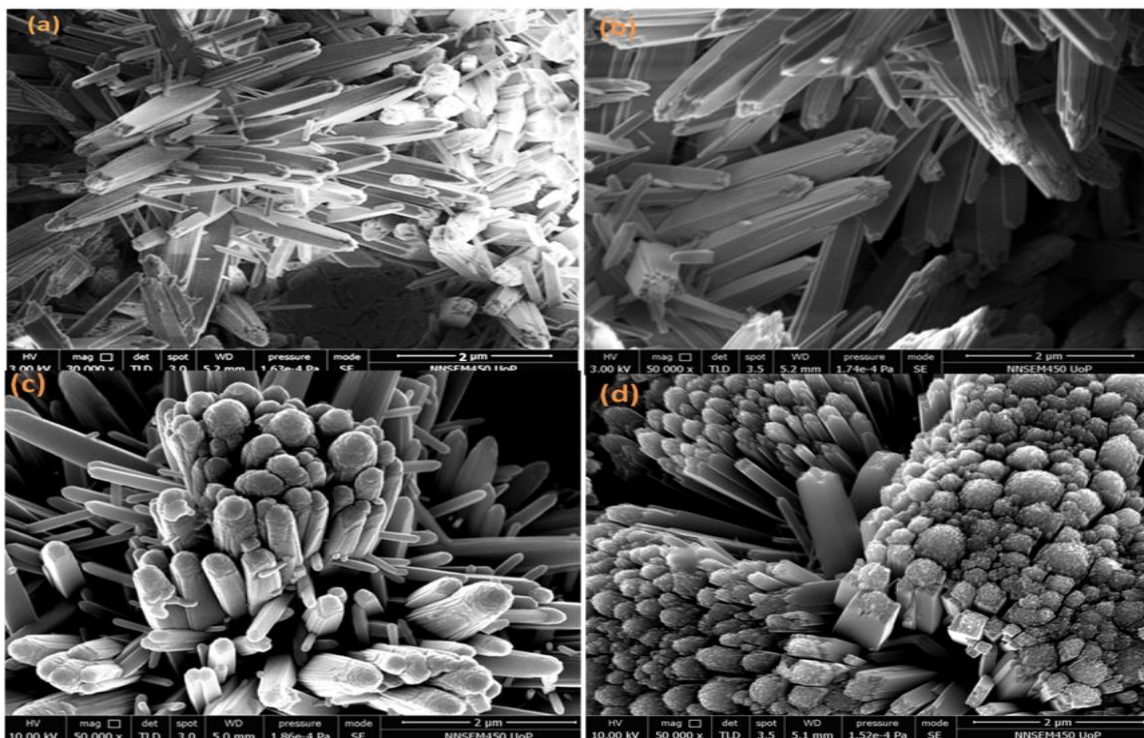


Figure 12 : FESEM of the TiO_2 films having deposition time (a) 4 hours, (b) 8 hours, (c) 12 hours and (d) 20 hours

FESEM images of TiO_2 microsphere films were shown in figure 12. It was clear that the films were formed on the surface of FTO glass. To get insight into formation mechanism of hierarchical microstructure, the TiO_2 film, having deposition time 4 hours, shows some voids on the substrate. Figure 12 (b) shows thin and short TiO_2 nanobridges which become bigger and longer. The surface morphology of the deposited film is uniform. However, increasing the time of deposition from 12 hours to 20 hours tend to form a cracked films. The possible reason to explain this phenomenon is increasing the time of deposition may decrease the adhesive force of TiO_2 on the FTO. Additionally, the heating and cooling process during the formation of TiO_2 was naturally carried out without adjusting the heating rate. Figure 12 (d) shows that for deposition

time of 20 hours, TiO_2 thin film is piled up from the substrate and uniformity of the film structure was not observed. Moreover, the mechanical strength of the film is so weak that the film sheds from the glass substrate easily.

(C) OPTICAL ANALYSIS

Figure 13 (a) shows the UV-Vis spectra of as-deposited TiO_2 thin films in the wavelength range of 300 to 800 nm. A strong and sharp UV edge was seen in all films deposited for different duration of time. The absorbance in the visible range was changed with increase in time of deposition.

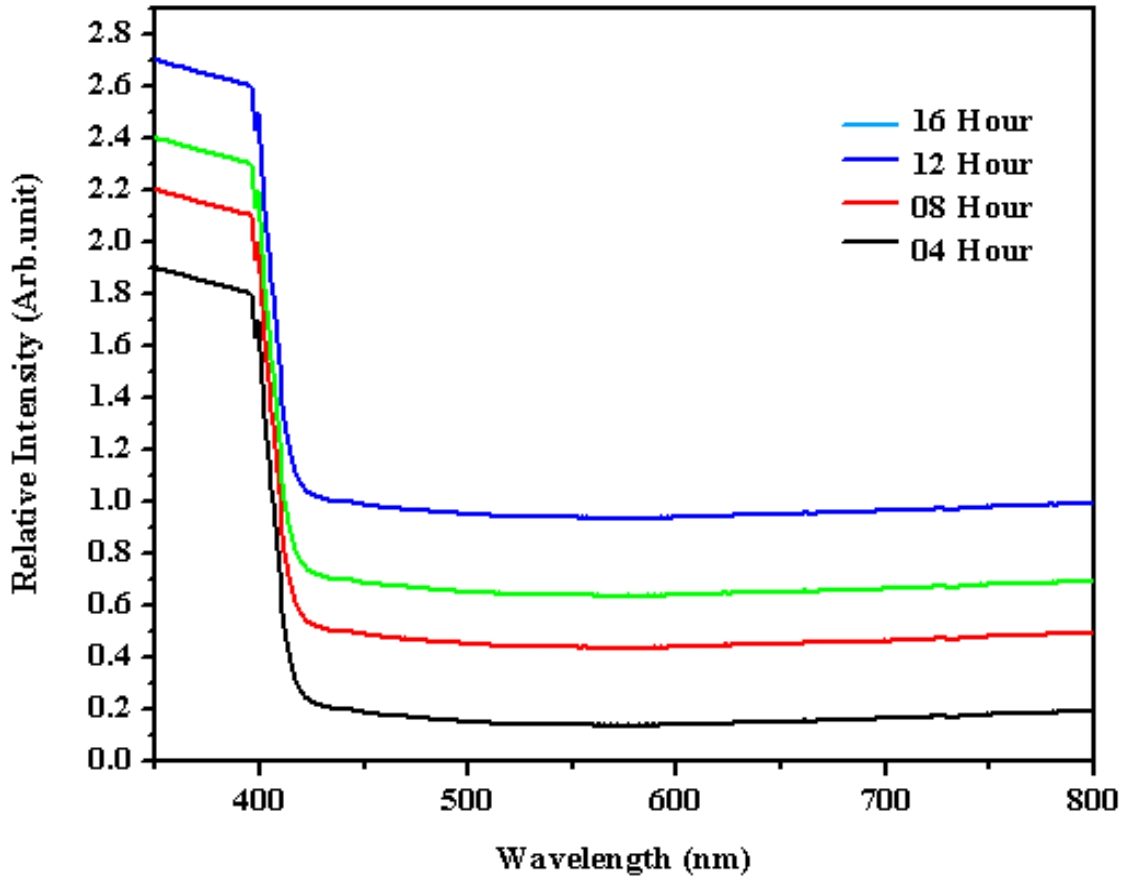


Figure 13 (a) : UV–Vis absorbance spectra of rutile TiO_2 for different time of deposition.

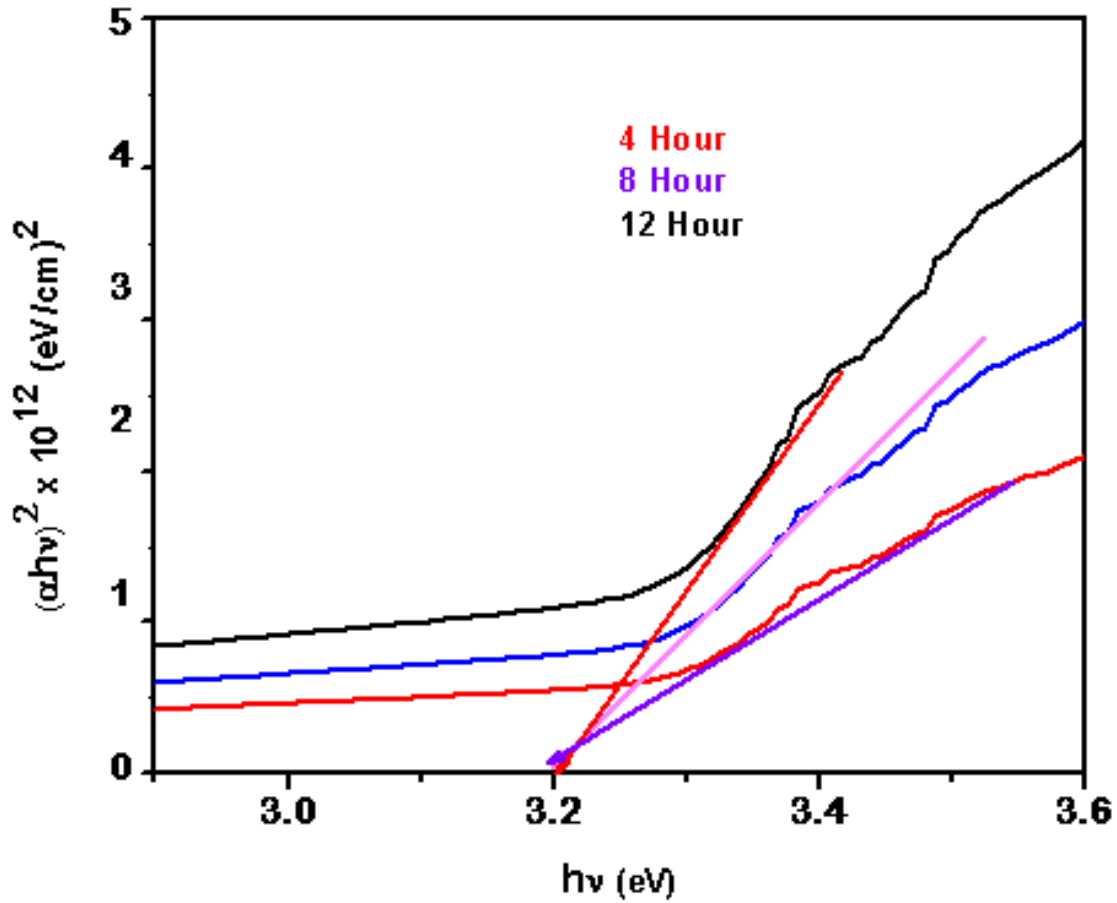


Figure 13 (b) : Band gap energy of rutile TiO₂ for different time of deposition.

The band gap energy calculated by using Tauc relation between absorption coefficient (α) and optical band gap (E_g) is

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

The optical band gap of TiO₂ thin films were calculated by extrapolating the linear portions of the curves from the plot of $(\alpha h\nu)^2$ versus $h\nu$. There was no significant changes observed in band gap value of TiO₂ films and it was 3.2 eV.

4. STUDY OF OPTIMIZED TiO₂ THIN FILMS

In the previous experimental work, we have seen that the densely aligned TiO₂ thin films can be prepared with different amount of titanium butoxide precursor solution, hydrothermal reaction temperature and deposition time. Thus, during deposition of TiO₂ thin films, the aim was to obtain highly uniform and high surface area of rutile TiO₂ thin films on FTO substrate at optimized process parameters.

(A) OPTIMIZED CONDITIONS OF TiO₂ THIN FILMS

The optimised process parameters for good quality and densely aligned TiO₂ thin films are summarised in the following table.

Precursor used	Solvent	Reaction Temperature	Quantity of Solution	Deposition Time	Amount of Precursor
Tetra butyl titanate (C ₁₆ H ₃₆ O ₄ Ti)	Double distilled water and HCl (1:1 volume ratio)	160 °C	60 ml	8 hours	0.75 ml

(B) X-RAY DIFFRACTION

The XRD pattern (θ - 2θ) of TiO₂ film deposited on conducting fluorine doped tin oxide glass substrate with all above optimized parameters is shown in the figure 14. TiO₂ film had preferred orientation along (101), (002) and (202) peak with its crystallographic axis revealing tetragonal rutile TiO₂ crystal structure. The peaks denoted by stars belong to FTO substrate. The intensity of (002) peak was strong. From the XRD pattern 2θ and β -FWHM values of (002) diffraction peak were obtained and it is observed that they are 31.45 ° and 0.2645 ° respectively. Using the values of θ and β , crystallite size was estimated.

Sample	FWHM (β) deg.	θ deg.	Crystalline size (nm)	Band gap Energy
TiO ₂	0.2645	31.45	35.3	3.2 eV

The average crystallite size was estimated from the full width at half maximum (FWHM) using Debye-Scherrer's formula. The average crystalline size was found to be 35.3 nm.

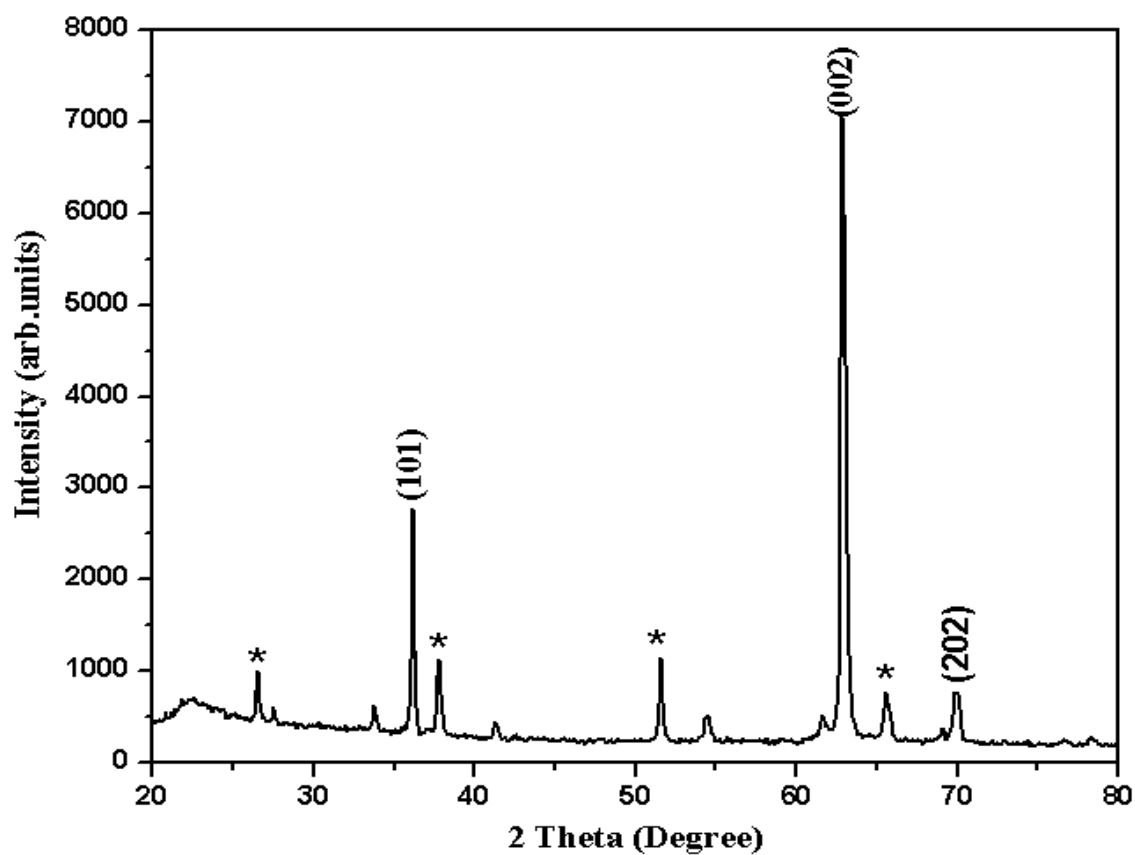


Figure 14 : XRD spectrum of optimised TiO₂ film prepared with amount of precursor 0.75 ml, time for deposition 8 hours and reaction temperature 160 °C

(C) XPS ANALYSIS

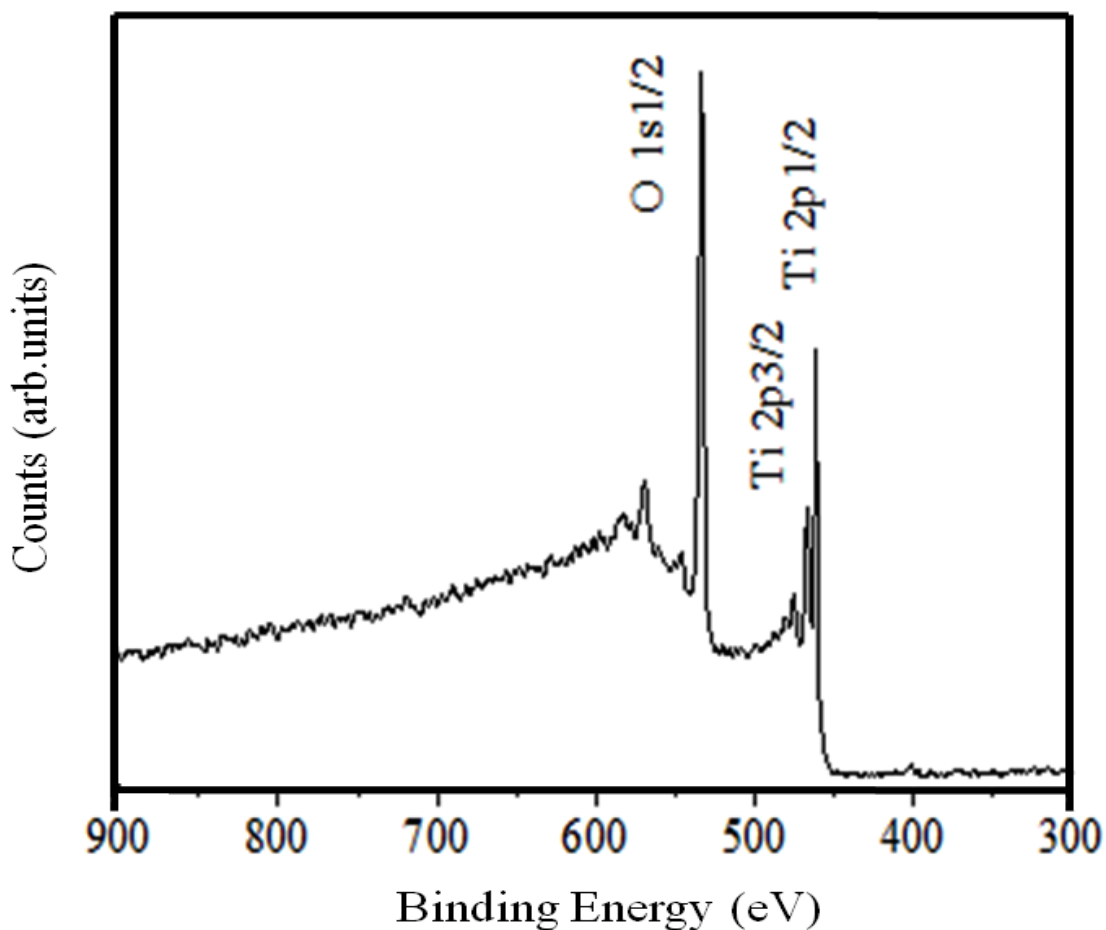


Figure 15 : XPS analysis of optimized TiO₂ thin film.

XPS is a commonly and widely used technique for surface analysis due to its simplicity in use and data interpretation. The XPS spectrum in Figure 15 confirmed O 1s1/2 peak with binding energy of 530.02 eV, which is assigned to the O 1s1/2 of TiO₂. The Ti 2p1/2 and Ti 2p3/2 peaks were obtained at 460.53 and 465.92 eV, respectively, which were closely matched to that reported elsewhere [16]. The obtained elemental Ti 2p1/2 and Ti 2p3/2 peaks shifted toward binding energies higher than 455 and 461 eV,

while the obtained O 1s_{1/2} peak shifted toward a low binding energy (530.02 eV) when compared with pure Ti [17].

(D) FIELD EMISSION SCANNING ELECTRON MICROSCOPY

Field emission scanning electron microscopy (FESEM) is a convenient technique to study the microstructure of thin films. Figure 16 shows the surface morphology of as-deposited TiO₂ thin film under different magnifications. A highly uniform growth with excellent TiO₂ nanoparticles coverage can be seen clearly. The hydrothermal processing parameter modifies to enable such growth. The TiO₂ film was uniform and covered well onto the FTO substrate. The fig.16 (a) revealed that optimized TiO₂ thin film was adsorbed onto the FTO substrate. Fig.16 (b) shows nanoflowers with rod-petals at lower magnification. The average length of the rod-petals is about 2-3 μm and average diameter is about 200-400 nm. Fig.16 (c) indicates cross-section of the TiO₂ film was densely aligned with average thickness of $\sim 4.1 \mu\text{m}$ on entire surface of the FTO substrate. Fig.16 (d) peaks show the elemental analysis of the film found from the energy dispersive X-ray spectroscopy (EDAX). It confirms the presence of titanium and oxygen elements. While tin element is due to the FTO substrate.

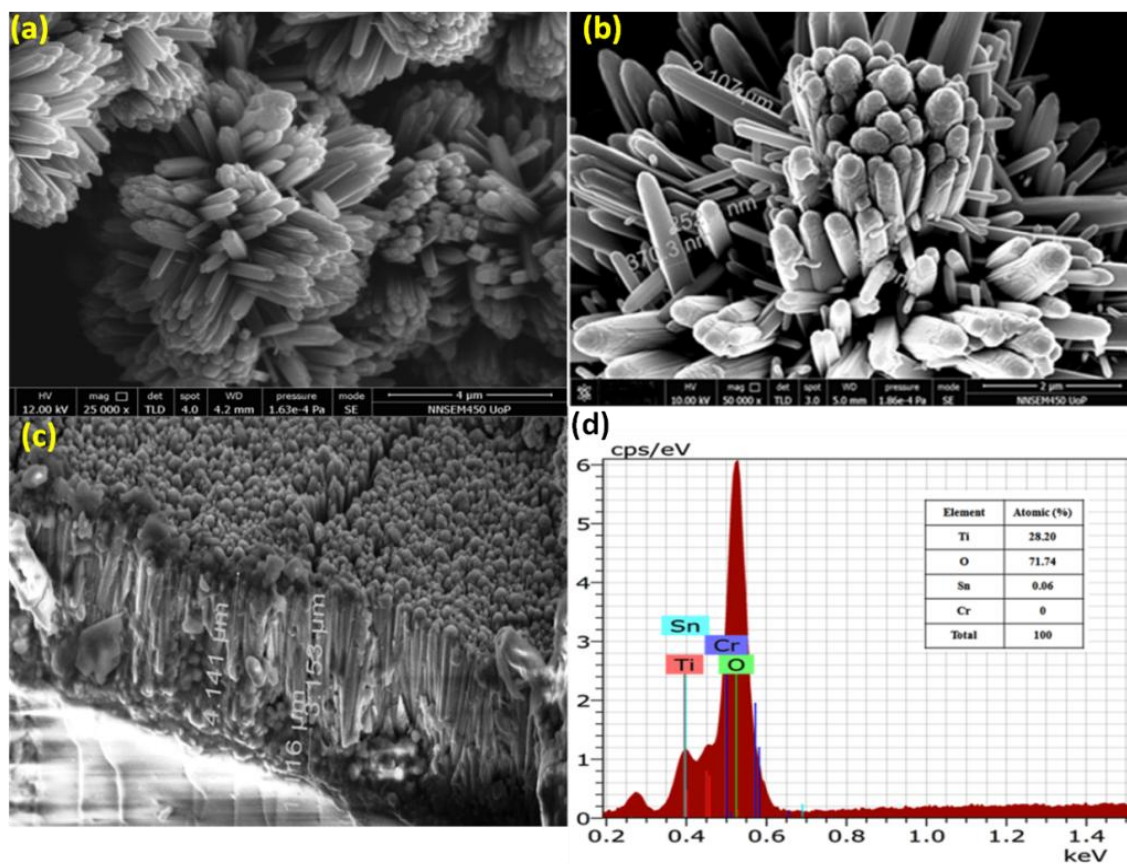


Figure16 (a b) : FESEM images of the sample at different magnifications,
Fig. (c) Cross-sectional view of the sample Fig. (d) elemental
analysis of the optimized sample from EDAX.

(E) TRANSMISSION ELECTRON MICROSCOPY (TEM) AND SAED RESULTS

TEM was used to examine the particle size, crystallinity and morphology of samples. Figure 17 (A,B) shows the low resolution TEM images of these nanoplates. Nanoplates of 20 nm in lengths were noticed in the bottom corner of TEM image. From close inspection (Figure 17 A) one can conclude that these nanoplates were composed of several nanometer sized crystallites. The SAED image pattern of rutile TiO_2 nanoplates is presented in Figure 17 (B). A set of rings instead of spots is observed due to random

orientation of the nanocrystallites inside the nanoplates, corresponding to diffraction from different planes of the nanocrystallites. The location of (101), (111) and (002) planes corresponding to 2.48, 2.18 and 1.47 Å interplaner spacing which are in good agreement with the same JCPDS No.((21-1272) used for XRD analysis. It confirms the formation of rutile phase as the rings correspond to specific rutile lattice planes of the nanocrystallites of TiO₂.

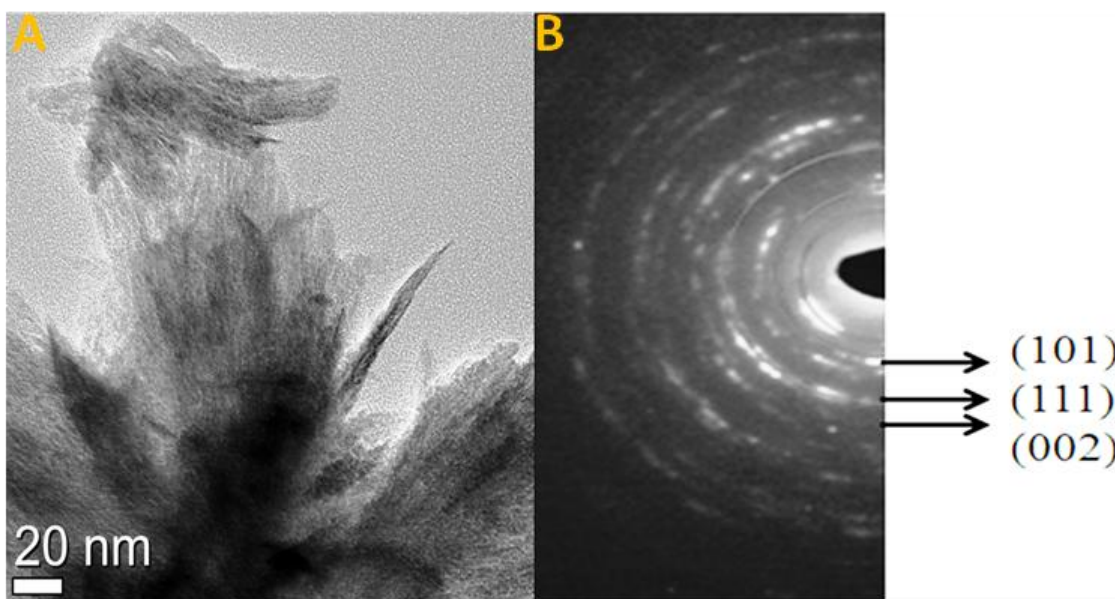


Figure 17 : TEM images of rutile nanoplates synthesized by hydrothermal method and SAED pattern of optimized rutile TiO₂ thin film.

(F) OPTICAL ANALYSIS

UV–Vis spectrum is considered as the most reliable technique to measure the band gaps of TiO₂. Fig.18 shows the absorbance spectra of TiO₂ thin films in 350–600 nm wavelength range. The large band gap of TiO₂ 3 eV for rutile requires an excitation wavelength that falls in the UV region. Light absorption in the visible region may be due to defect formation in the crystal. The band gap values of TiO₂ thin films were estimated by extrapolating the linear portion of the Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$.

The calculated band gap value for TiO₂ film was 3.2 eV. Maximum absorption and the absorption band edge can be estimated to be around 350 and 400 nm, respectively.

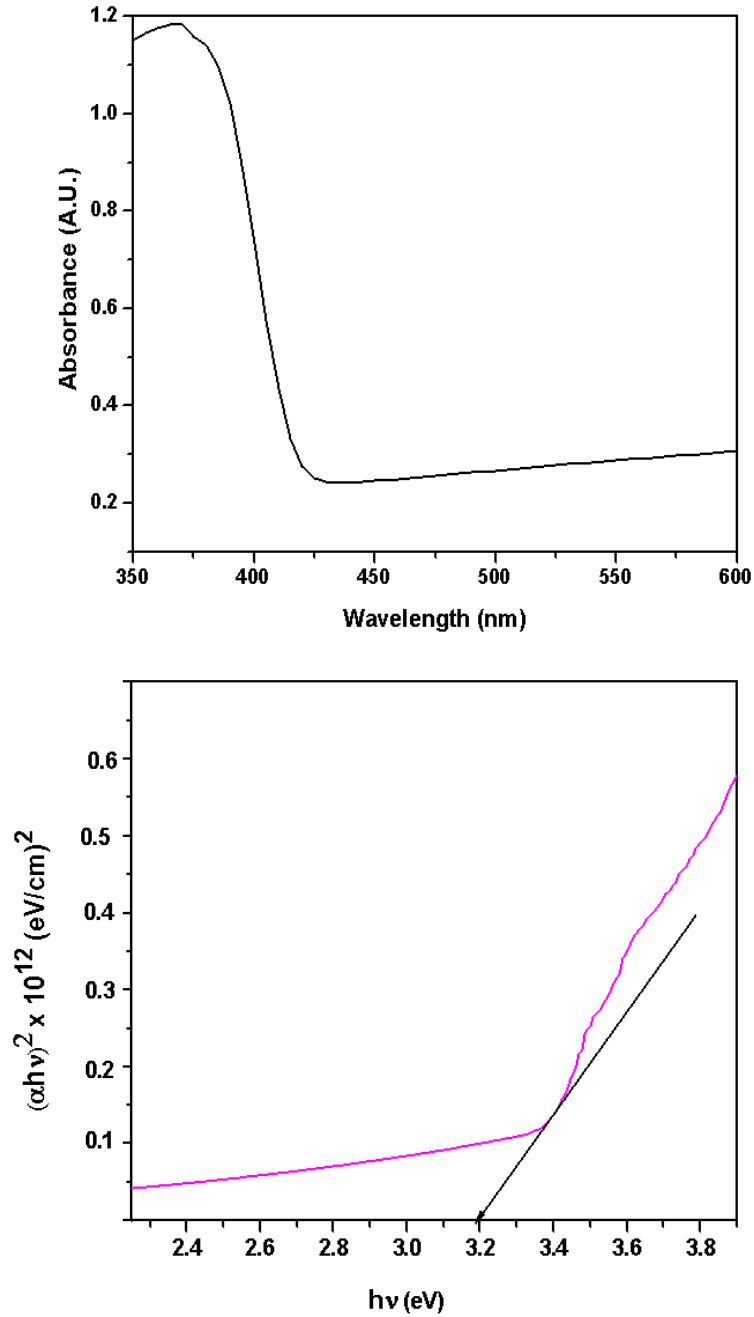


Figure 18 : UV-Vis spectrum and $(\alpha h\nu)^2$ vs $h\nu$ graph for TiO₂ thin film prepared with amount of precursor 0.75 ml, time for deposition 8 hours and reaction temperature 160 °C

(G) FTIR SPECTROSCOPY

The FTIR spectra of the prepared TiO_2 thin film was shown in fig.19. The spectra were taken in the range from 4000 to 500 cm^{-1} . Several peaks related to TiO_2 are observed in hydrothermally deposited film. A strong and wide absorption band of TiO_2 immergence in range 1962 to 1060 cm^{-1} which is due to the vibration of Ti-O- Ti bonds in TiO_2 lattice. The peaks at 1546 cm^{-1} and the broad peaks appearing at 3100–3600 cm^{-1} are assigned due to vibrations of hydroxyl groups [56].

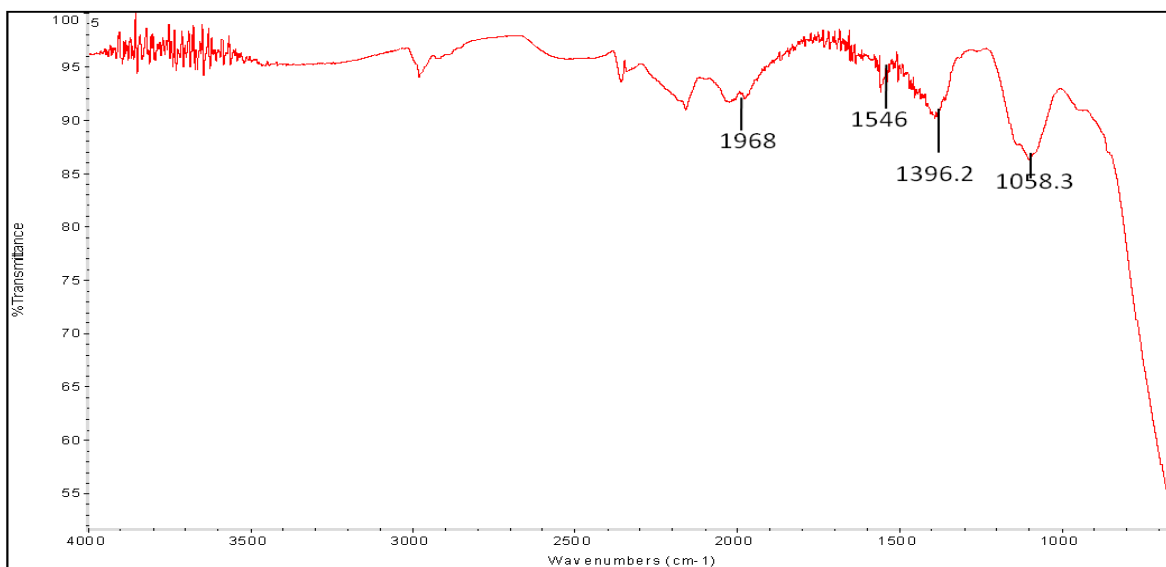


Figure 19 : FTIR spectrum of optimized TiO_2 thin film.

4.1 PREPARATION OF WORKING ELECTRODE

The TiO_2 electrode, where the sunlight is absorbed, is called the working electrode.

a) CLEANING

In hydrothermal deposition method, extreme cleanliness of the substrate is essential. If surfaces of the substrates are contaminated then nucleation sites facilitating growth resulting into non-uniform, porous and non-adherent film. The cleaning process includes

- a. Sonicate in soap solution – 15 min.
- b. Rinse with deionized (DI) water.
- c. Sonication in Acetone – 10 min
- d. Sonication in Isopropanol – 10 min
- e. Finally, the substrates are dried

b) PREPARATION

In the first set of experiment, we have optimized TiO_2 films by varying one of the parameters and keeping other process parameters constant. The optimal process parameters obtained from previous section were considered for fabrication of working electrode.

The TiO_2 array was deposited on FTO using a hydrothermal method reported previously by Liu and Aydil [50]. In our experiment, tetra butyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) and hydrochloric acid (HCl, 38%) of analytical grade were used without further purification. Double distilled water was used throughout the preparation. The typical experimental procedure is depicted as follows: First 0.75 ml of tetra butyl titanate was added into mixture of the equal amount double distilled water and concentrated hydrochloric acid. After stirring at ambient conditions for 0.5 hour, the solution became clear and transparent. Here the tetra butyl titanate was used as the precursor for the growth of TiO_2 arrays and the HCl was used to avoid the hydrolysis of the precursor. A FTO substrate was loaded in the autoclave with the conducting side facing up. The resulting solution

was then transferred into a 100 ml Teflon-lined stainless steel autoclave and sealed properly. The hydrothermal reaction was conducted at 160 °C for 8 hours. After the synthesis, the autoclave was cooled down naturally to room temperature. FTO substrate covered with TiO₂ was taken out, rinsed with deionised (DI) water and then dried in an electric oven. It was then annealed at 450 °C in air for 30 min.

5. QUANTUM DOT SENSITISED SOLAR CELL

In the first set of experiment, we have optimized TiO_2 films by varying one of the parameters by keeping other process parameters constant. The optimal process parameters obtained from previous section were considered for fabrication of working electrode and quantum dot sensitized solar cell.

As mentioned above, multiple sensitization techniques have been developed for semiconductor sensitizers. One of the simplest is Successive Ion Layer Absorption and Reaction (SILAR). SILAR involves immersing a substrate into a solution with a desired precursor allowing this precursor ion to adsorb on the surface of the TiO_2 , then removing the sample, rinsing excess ions off and immersing in the other precursor ion. SILAR works if the reaction for the precursors is spontaneous, such as Cd^+ and S^{2-} . By using successive cycles SILAR is not able to have this control over the size of the sensitized layer so pre sensitized quantum dots allow for tailoring the cell to specific applications.

Deposition of CdS quantum dots using Successive Ionic Layer Adsorption and Reaction (SILAR) Method.

In this set of experiments, we have deposited CdS on titanium oxide films at various concentrations by keeping other process parameters constant. In a typical SILAR deposition cycle, Cd^{2+} ions were deposited from 0.05 M $\text{Cd}(\text{NO}_3)_2$ in ethanol solution and the sulphide source was 0.05 M Na_2S in methanol. Concentrations of Cd and S were varied from 0.01 M to 0.05 M. The conductive FTO glass, pre-grown with TiO_2 nano-branched arrays was dipped into the $\text{Cd}(\text{NO}_3)_2$ ethanol solution for 2 min, rinsed with ethanol and then dipped into a Na_2S solution for another 2 min, rinsed again with methanol. The two-step dipping procedure is termed as one SILAR cycle and the incorporated amount of CdS can be increased by repeating the assembly cycles. The whole experiment was conducted at room temperature (18 – 20°C). The entire SILAR process to obtain the CdS quantum dots is as shown in figure 20.

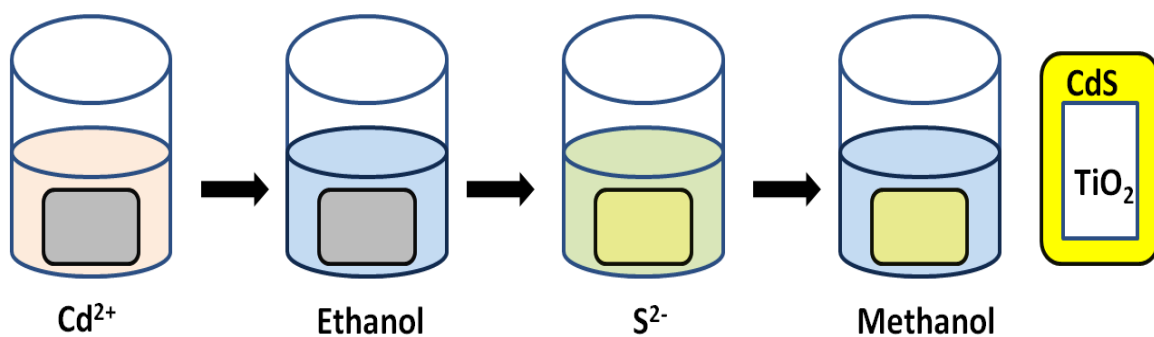


Figure 20 : SILAR process to obtain the CdS quantum dots.

The structural property of the CdS sensitized TiO_2 thin film was characterized by using X-ray diffraction analysis. The surface morphology was investigated by using FESEM analysis and optical properties by using UV-Vis spectroscopy.

(A) X-RAY DIFFRACTION

The XRD pattern of TiO_2 thin film deposited by hydrothermal method and sensitized with CdS by using Successive Ionic Layer Adsorption and Reaction (SILAR) method is shown in Fig. 21.

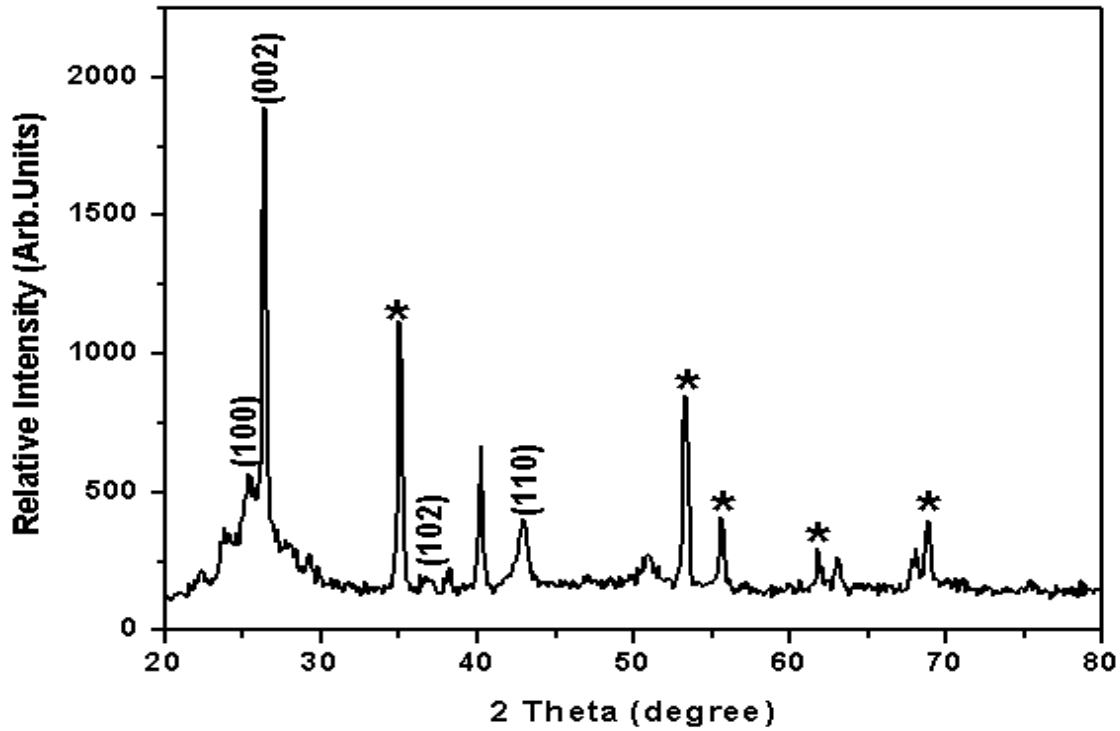


Figure 21 : XRD pattern of CdS sensitized TiO₂ sample.

The cadmium sulphide phase was obtained by comparing with the standard JCPDS data card no. 80-0006. The synthesized CdS nanoparticles exhibited hexagonal crystal structure. The high intense reflection peak was observed at $2\theta = 26.48^\circ$ corresponding to the hexagonal (002) plane. The other peaks were indexed at $2\theta = 25.24^\circ$, 26.48° , 40.22° , 43.94° etc. and the planes were marked as (100), (002), (102) and (110) respectively. The average crystallite size was estimated from the full width at half maximum (FWHM) data using Debye-Scherrer's formula [64].

$$\text{Crystallite size} = \frac{0.9\lambda}{\beta \cos \theta}$$

Moreover, we can see the diffraction peaks of CdS are broadened which may be due to the smaller crystalline sizes of the CdS Quantum Dots. The average crystallite size

corresponding to the (002) plane of CdS nanoparticles was calculated and found to be 38.4 nm.

(B) FESEM ANALYSIS

The radially distributed nanoflakes are just like the petals in a natural chrysanthemum-flower structure with a thickness of several nanometers. Figure 22 (A) show FESEM image of TiO_2 deposited on entire surface of FTO substrate. Fig.22 (B) shows the FESEM image of the microscopic structure of the CdS.

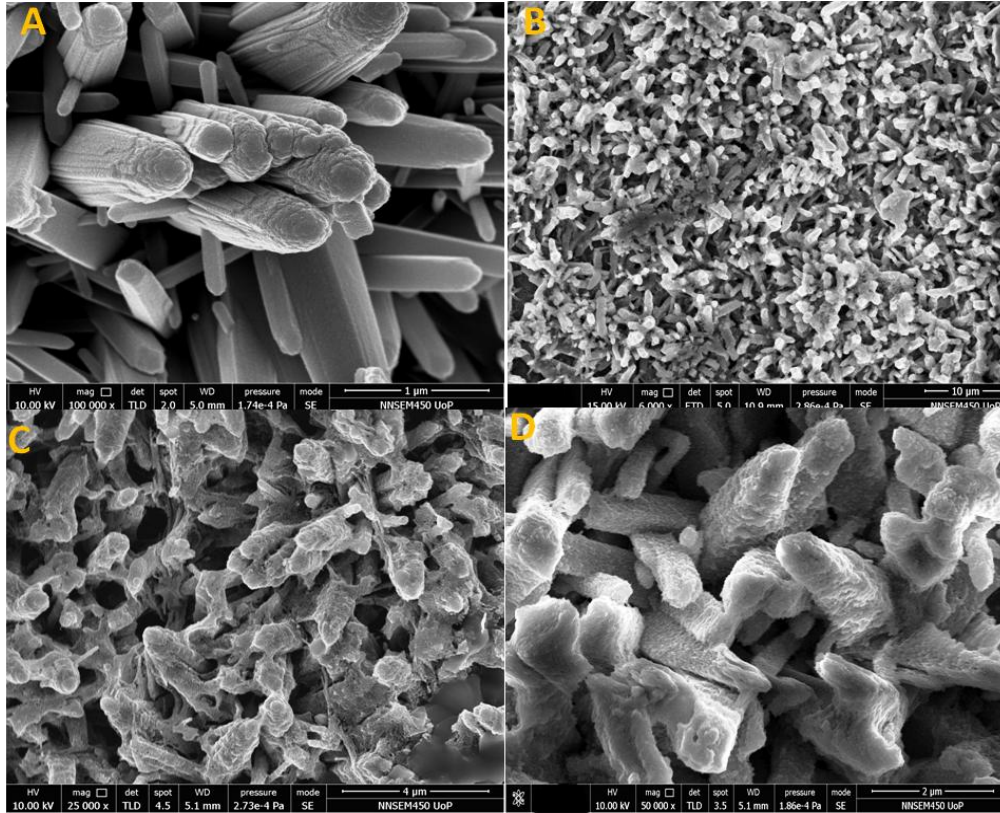


Figure 22 : (A) FESEM images of TiO_2 nanorod arrays on FTO-coated glass substrates (B, C, D) represent the morphology of TiO_2 films sensitized with different molar concentration of CdS.

Quantum Dot was further deposited at 0.01 M CdS. The CdS/TiO₂ shows that large aggregates of CdS cover the entire surface of the TiO₂. Fig. 23 (C, D) shows CdS deposited at 0.03 M and 0.05 M suggesting that the CdS QDs are grown homogeneously onto TiO₂ hierarchical nanostructures.

It indicates that the CdS QDs were coated over the branches uniformly, which is crucial for obtaining good PEC properties. After deposition of CdS as shown in Fig. 22 B, the surface of TiO₂ nanorods became rough, indicating that the deposition of CdS is on the TiO₂ nanorod arrays.

Figure 23 (A,B,C) show the FESEM morphologies of the CdS/TiO₂ the elemental energy-dispersive spectroscopy (EDS) mapping characterization. It was used to investigate the chemical composition component and elemental distribution of the CdS/TiO₂.

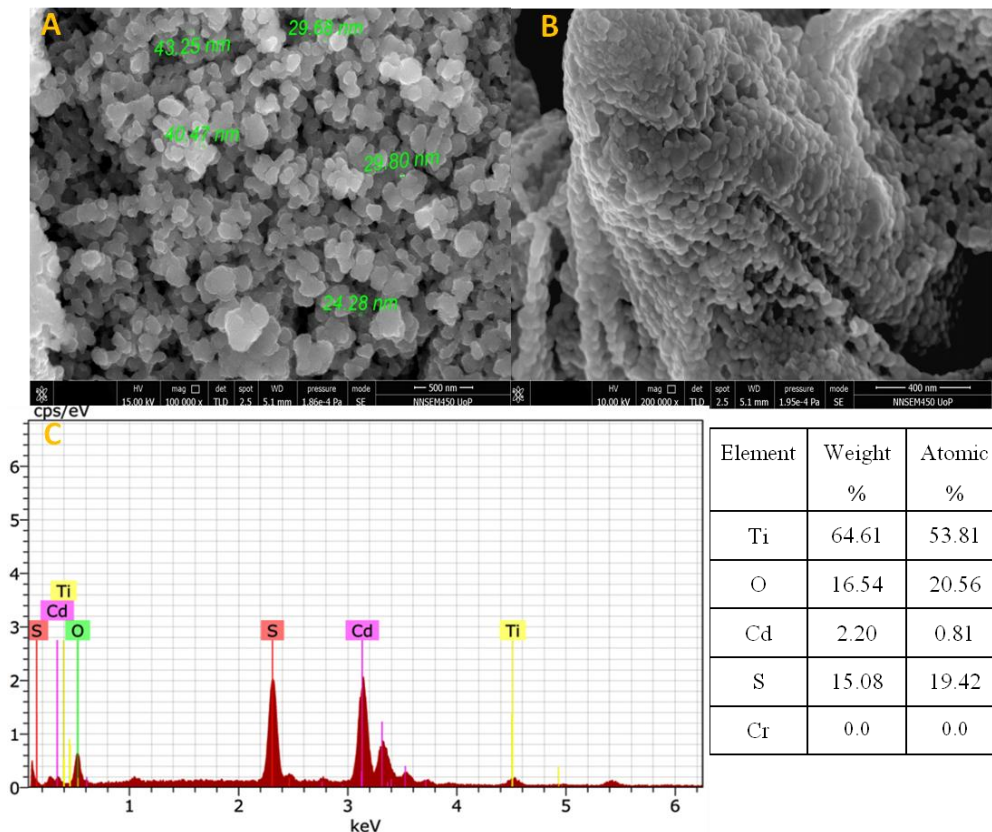


Figure 23 (A, B) : FESEM images of CdS with high resolution and (C) EDAX spectra of CdS sensitized TiO₂

Fig.23 (A) shows a low magnification FESEM image of the CdS/TiO₂ sample. In order to confirm the formation of CdS on TiO₂, we also took EDAX, which shows the peaks Ti, O, Cd and S elements are homogenously distributed among the whole CdS/TiO₂ hierarchical surface. As it is well known that the QD loading amount is closely related to the specific surface area of TiO₂. The mesoporous TiO₂ film is expected to allow higher QD loading in view of the higher surface area.

(C) OPTICAL ANALYSIS

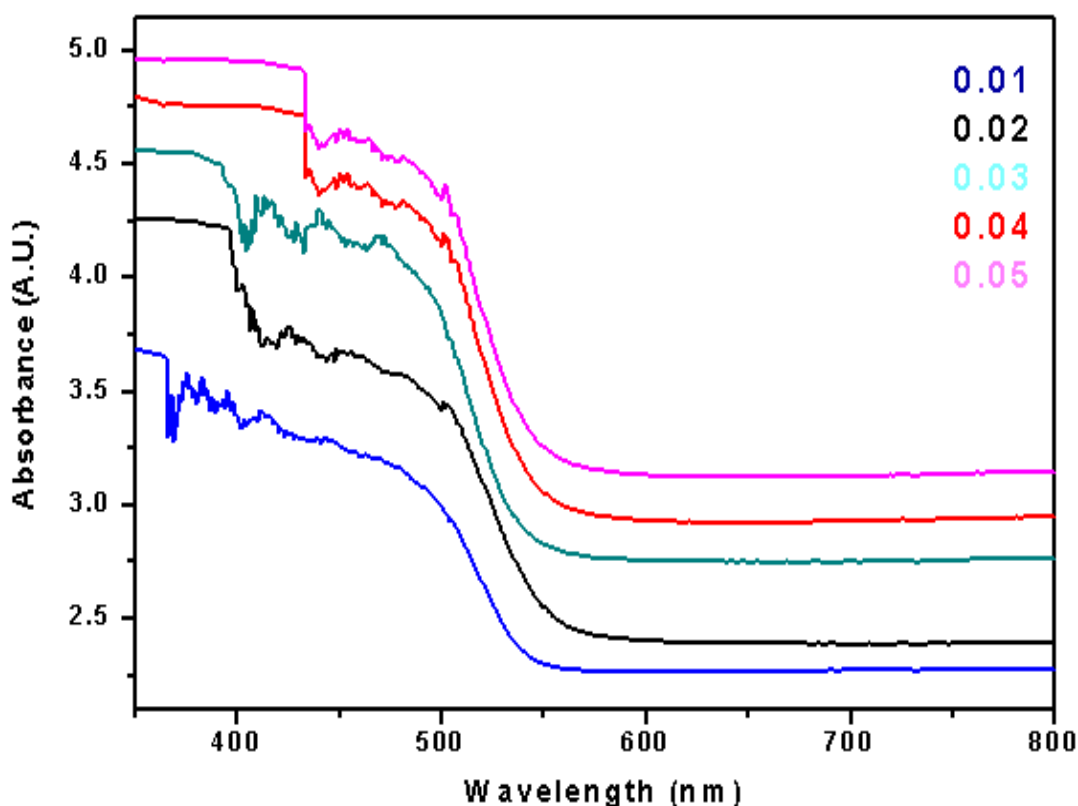


Figure 24 : Absorbance spectra of different molar concentration of CdS.

Figure 24 shows the UV-Vis absorption spectra of photoanode with different molar concentration. The absorption in the visible region is remarkably enhanced in comparison with bare TiO₂, indicating the efficient photosensitization of CdS Quantum dots. The molar concentration effect on the FTO/TiO₂ electrode can

absorb only ultraviolet light with wavelength smaller than 410 nm. After formation of CdS Quantum dots on TiO₂ nanorods, the light absorbance extends to visible light region [18]. The absorbance of the spectra increases with an increase in different molar concentration of precursor solution, indicating an increased adsorption amount of CdS. It is found that all the photoanode films have strong absorbance from 400 nm to 550 nm. Furthermore, the formation of CdS Quantum dots sensitizers on TiO₂ nanorods can be desirable for light harvesting of solar energy. This result is the similar to those results as other reported [18–20].

UV–Vis absorption spectrum shows maximum peak at 380 nm, which is due to the size dependent electronic transitions in the CdS. For FTO/TiO₂/CdS electrodes, the light absorbance extends to visible light region, and the smaller CdS crystallites grow and aggregate into larger crystallites accompanied with the increased adsorption amount of CdS, but excessive growth and aggregation of CdS crystallites will increase the chance of the recombination of the photoelectrons and holes, which will result in the decrease of the photo electrochemical properties.

(D) CuS COUNTER ELECTRODE

Alternatively, the use of polysulfide electrolytes is to avoid corrosion losses has proven to be a better match for QDSSCs. CuS electrodes can provide relatively higher conductivity and electrocatalytic activity toward polysulfide electrolytes and exhibit potential application in QDSSCs [45].

CuS was also deposited on FTO electrodes by a SILAR method which is presented in Ref. [44]. Precursor solutions contained 0.5 M Cu (NO₃)₂.xH₂O in methanol and 1 M Na₂S.9H₂O in 1:1 water and methanol mixture. A well cleaned FTO electrode was immersed for 5 min in the metal salt solution, then copiously washed with distilled water and dried in an air then immersed for 5 min in the Na₂S.9H₂O solution and finally washed and dried again. This sequence again corresponds to one SILAR cycle. 10 SILAR cycles were performed. Finally, the electrode with deposited CuS film was first dried in an air and then it was put for a few minutes in an oven at 100 °C.

(E) QUANTUM DOT SOLAR CELL FABRICATION

The CdS QDs-adsorbed TiO₂ electrodes and Counter electrode were assembled in a sandwich type cell. A 50 µm Surlyn film was used as a spacer to separate the electrodes. Polysulfide electrolyte consisting of 0.5 M Na₂S, 2 M S and 0.2 M KCl in water to methanol volume ratio of 3:7 was used as a redox electrolyte.

The photocurrent-voltage (J-V) measurements were carried out by a Keithley 2420 source meter when the cells were irradiated by a solar simulator under AM 1.5 G illumination of (100 mW cm⁻²). The photovoltaic performance, fill factor (*FF*) and power conversion efficiency (η) of QDSSCs were calculated according to the following equations [55].

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}}$$

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\%$$

where P_{max} is the maximum power output, P_{in} is the incident light power, J_{sc} is the short-circuit current density (mA/cm²), V_{oc} is the open circuit voltage (V), J_{max} (mA/cm²) and V_{max} (V) are the current density and the voltage at the point of maximum power output in the J-V curves, respectively.

(F) **CURRENT-ELECTRIC POTENTIAL CHARACTERISTICS OF SOLAR CELLS MADE WITH THE ABOVE PHOTOANODES AND COUNTER ELECTRODES**

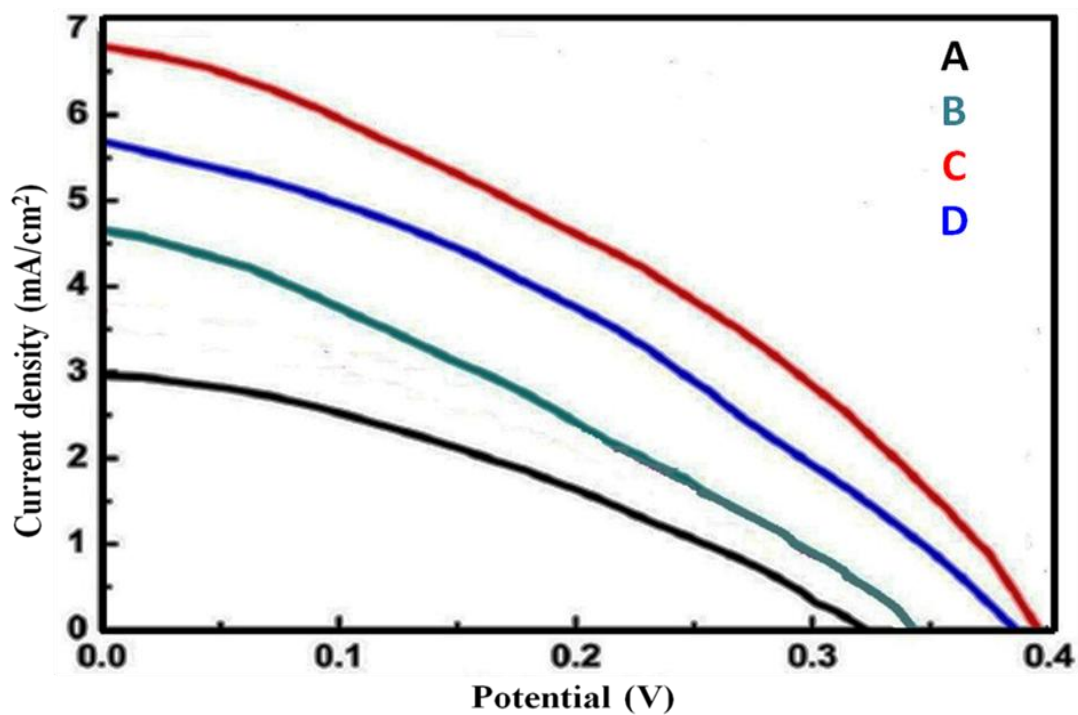


Figure 25 : Characteristic of different amount molarity of CdS sensitized under AM 1.5 G solar simulator illuminations

Table 2 : Variation in efficiencies for different molar concentrations of CdS

Sample	Molarities of CdS (M)	J_{SC} (mA-cm ⁻²)	V_{OC} (V)	FF	η %
A	0.02	3.02	0.32	0.33	0.32
B	0.03	4.61	0.34	0.32	0.51
C	0.04	6.76	0.38	0.37	0.95
D	0.05	5.64	0.37	0.35	0.73

Fig.25 shows the J-V plot for the different samples prepared at different molar concentrations. Table 2 shows variation in efficiencies for different molarities of CdS. The measurement process follows a similar approach to that discussed in [46]. The short circuit current density (J_{sc}) of the cells was increased from 3.02 to 6.76 $\text{mA}\cdot\text{cm}^{-2}$ as the molarity of CdS increased from 0.02 M to 0.05 M. Correspondingly the cell conversion efficiency of quantum dot solar cell is increased from 0.32 to 0.95 %. However J_{sc} was decreased to 5.64 $\text{mA}\cdot\text{cm}^{-2}$ when molarity of CdS was 0.05 M. This means when molarity of CdS was reached to the value of 0.04 M, we get highest conversion efficiency of 0.95 %. Efficiency was decreased when we increase further molar concentration. A power conversion efficiency of 0.95% was obtained for the TiO_2 sample with nano branched structures grown in TiCl_4 solution and sensitized with 0.04 M CdS. From the above results, it is clear that solar cells with CdS quantum dots were deposited on the TiO_2 film and it improves photovoltaic performance.

6. DYE SENSITIZED SOLAR CELL (TiCl₄ TREATMENT)

The titanium dioxide layer is one of the main components of DSSC, which is conventionally prepared in the first set of experiment. We have considered TiO₂ films from previous section for fabrication of working electrode and Dye sensitized solar cell.

A) DYE SOLUTION

The dye used in the study was cis-diisothiocyanato-bis (2, 2'-bipyridyl-4, 4'-dicarboxylato) ruthenium (II) bis (tetra-butyl ammonium) (i.e. N719, Sigma Aldrich).

The dye solution (0.3 mM) was prepared in acetonitrile (CH₃CN) and ethanol alcohol as solvents in equal proportion. The solution was stirred for 30 min and stored in sealed container for 24 hours before use. The dye solution is always needed to be stored away from light. Subsequently, the surface-treated TiO₂ working electrode was immersed in the dye solutions and then kept overnight at room temperature to adsorb the dye onto the TiO₂ surface. They are kept in the dye until being used in a cell.

B) PREPARATION OF COUNTER ELECTRODE

Two 0.8 mm diameter holes were made on a piece of 2×2 cm² FTO glass. The cleaned substrate is heated for 15 min at 450°C to remove the residual organic contaminants. A thin layer of platinum (Pt) was deposited on the FTO glass by doctor blading (for the Platisol T/SP paste). The solution is light sensitive. The electrode was heated immediately at 450°C for 15 min, activating the platinum layer for working. The activated electrodes were instantly used for cell making.

C) ELECTROLYTE SOLUTION

Iodolyte AN-50 is a high performance volatile electrolyte that helps to maximize the performance of dye-sensitized solar cells. A few drops of Iodolyte AN-50 are typically used to fill the space between the photo-anode and cathode of small surface area of the test cells. Place a drop of electrolyte on the filling hole and place the cell in a vacuum chamber.

D) CELL FABRICATION

Upon dye sensitization, the TiO_2 electrode was assembled into a sandwich like structure with the Pt-counter electrode. A square gasket was cut into the sealant spacer material Meltonix (1170-60). The inner dimensions should match with the Titania film, and the outer dimensions should be 3 mm bigger on all four sides. The working electrode was taken out of the dye solution and carefully rinsed with ethanol. The sealant gasket was placed around and the counter electrode was put on it while the Pt film faces the Titania. Heating at 120 °C would seal the electrodes. The electrolyte solution was inserted through one of the holes in such way that there is no air bubble inside. The glass surface was cleaned with acetone then it was wiped and the holes were sealed with another piece of sealant and a cover glass. The space left for contact was painted with silver paint to make better contact. Now the solar cell is ready to work.

(E) TiCl_4 POST-TREATMENT

Solar cell performance has been improved mainly by controlling the surface morphology. Post treatment of mesoporous TiO_2 films with TiCl_4 solution has been used to increase the efficiencies of the cells [47]. TiCl_4 surface treatment improves the inter particle connectivity. TiCl_4 surface treatment has been reported to increase surface area and improve electron transport, light scattering of TiO_2 and anchoring of dyes [48]. Although the treatment's effect strongly depends on the starting of TiO_2 material to which it is applied. The TiCl_4 surface treatment's effects on the morphologies of the TiO_2 films were studied in terms of dye adsorption, charge transport, and electron lifetime. We found that TiCl_4 treatment had fewer defects, which led to relatively faster electron transport and enhanced electron lifetime. As a result, a DSSC containing TiCl_4 treated TiO_2 thin films exhibited enhanced overall energy conversion efficiency as compared with a DSSC without TiCl_4 treated thin film.

TiCl_4 reacts with water in an exothermic reaction, heating up the solution while making. Moreover, at higher temperature (even at room temperature) it oxidizes into TiO_2 . TiCl_4 solution was prepared by adding 2 ml TiCl_4 into a mixture of 50 gm of ice and 50 gm of water. Prior to dye adsorption, TiO_2 films were immersed in TiCl_4 aqueous

solution in a beaker and then kept in an oil bath at 70°C for 30 min. After flushing with ethanol and drying, the electrodes were sintered again at 450⁰ C for 30 min.

6.1 CURRENT-ELECTRIC POTENTIAL CHARACTERISTICS OF SOLAR CELLS MADE WITH THE ABOVE PHOTOANODES AND COUNTER ELECTRODES.

The efficiency of prepared solar cell was estimated through I-V characterization which was measured with a Keithley 2400 source meter using an AM 1.5 (100 mW/cm²) solar simulator. The photovoltaic performance, fill factor (FF) and power conversion efficiency (η) of DSSCs was calculated according to the following equations [55].

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}}$$

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100\%$$

Where P_{max} is the maximum power output, P_{in} is the incident light power, J_{sc} is the short-circuit current density (mA/cm²), V_{oc} is the open circuit voltage (V), J_{max} (mA/cm²) and V_{max} (V) are the current density and the voltage at the point of maximum power output in the J-V curves, respectively.

Fig. 26 shows the photocurrent density versus voltage characteristics of DSSCs, while the photovoltaic performance parameters of the cells are listed in table 1.

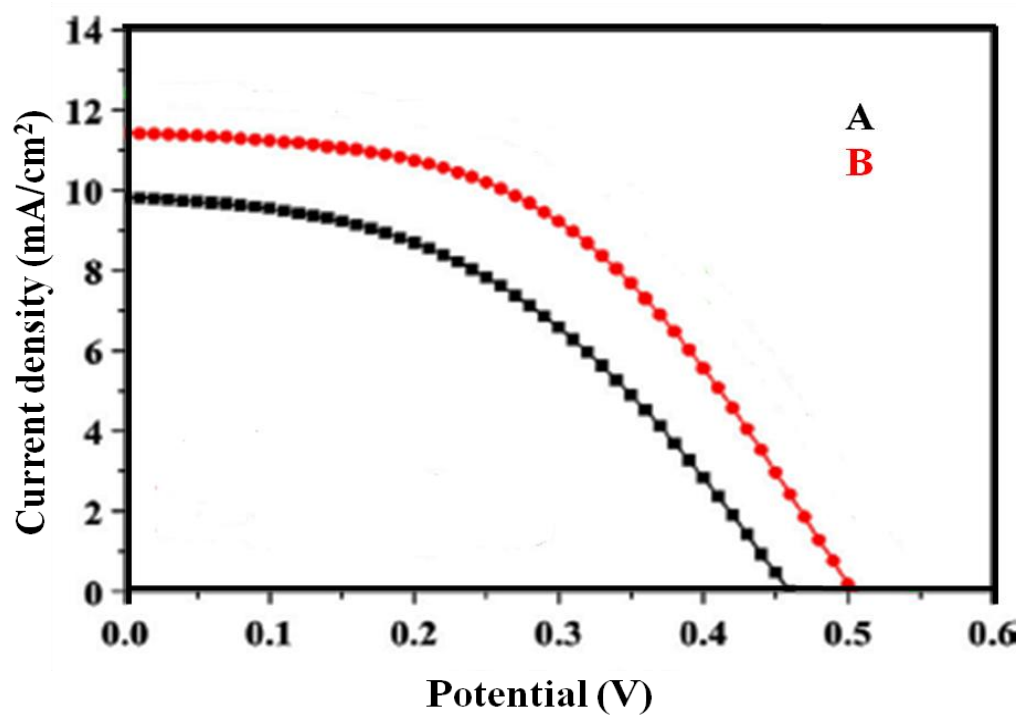


Figure 26 : J–V curves of TiO₂ (A) without TiCl₄ treatment and (B) with TiCl₄ treatment.

Table 1 : Photovoltaic performance parameters of the cell

Sample	Jsc (mA-cm ⁻²)	Voc (V)	FF	η (%)
A	9.81	0.46	0.44	1.98
B	11.42	0.51	0.47	2.73

For both before and after TiCl_4 post treatment the conversion efficiencies were determined. The working electrode without TiCl_4 treatment 5 μm thick layer of sensitized TiO_2 exhibits remarkable 1.98 % conversion efficiency and after TiCl_4 treatment it was found to be 2.73 %. TiCl_4 surface treatment was beneficial to increase the surface area of TiO_2 working electrode.

The value of the J_{sc} is increased from 9.81 to 11.42 $\text{mA}\cdot\text{cm}^{-2}$ with the photoanode changed from bare TiO_2 to that of FTO substrate by immersing in TiCl_4 solution. Correspondingly, the open circuit voltage (V_{oc}) increased from 0.46 V to 0.51 V. The main reason for increment of the J_{sc} is due to the improvement of dye adsorption in denser TiO_2 nanorod arrays grown on the TiCl_4 treated TiO_2 substrate. Due to TiCl_4 treatment there is increase in the amount of the adsorbed dye, electron transport, and electron lifetime. Hence the efficiency is increased from 1.98% to 2.73% after TiCl_4 treatment.

7. BOTTLE BRUSH LIKE DYE SENSITIZED RUTILE TiO₂ (EFFICIENT SOLAR CELL)

(a) Synthesis of TiO₂ bottle brush

The TiO₂ nanorods were synthesized using the technique [73], while the bottle brush sample was synthesized by same route but changing little experimental conditions. In a typical synthesis, titanium (IV) isopropoxide (0.5 mL) was added to an (1:0.9) volume of distilled water and concentrated HCl. The resulting mixture was stirred for 30 min. The clear transparent solution was then transferred to a Teflon liner stainless steel autoclave (25 mL), and a piece of glass was immersed in the solution parallel to the wall. The autoclave was sealed and placed in an oven at 170 °C for 9 hrs. Upon completion of the reaction, the autoclave was allowed to cool at room temperature naturally and the deposited film was subsequently washed in double distilled water, ethanol and finally dried at room temperature. The thickness of the resulting TiO₂ bottle brush and nanorods thin films was estimated using surface profiler (Ambios XP-1). It is observed that the deposited samples having thickness 4.2 μm.

(b) Characterizations

The surface morphologies of the prepared nanofibers samples were recorded by a scanning electron microscopy (SEM, JEOL JSM 6360, Japan) and Field emission scanning electron microscope (FESEM; S-4700, Hitachi). X-ray diffraction (XRD) measurements were carried out using a D/MAX Ultima III XRD spectrometer (Rigaku, Japan) with Cu K line of 1.5410 Å. Selected area electron diffraction (SAED) pattern, and high resolution transmission electron microscopy (HRTEM) images were obtained by TECNAI F20 Philips operated at 200 kV. Optical absorption studies of the films deposited samples were carried out in the wavelength range of 350–1,100 nm using UV–Vis spectrophotometer (Shimadzu-1800, Japan).

(c) Dye-sensitized solar cell assembly

The DSSCs properties were measured by Sol2A Oriel New Port Corporation USA, with Keithley-2420 source meter less than 1.5 AM illumination. The Iodolyte AN-50 (Solaronix) electrolyte was inserted through pre-drilled hole from Pt/FTO counter electrode. Finally, device was sealed using thermoplastic. For comparison, we used commercial P25 Degussa TiO₂ nanoparticles, and 4.2 μm thick film was fabricated by the well-known doctor blade technique. Briefly, 1 g of TiO₂ nanoparticles paste was prepared using ethyl cellulose, lauric acid, and terpenol in ethanolic solution; and a film was deposited on the FTO-coated glass substrate and annealed at 450 °C for 5 min. The deposited film was loaded with 0.3 mM N3-dye molecules by dipping the substrate for 24 hrs in ethanolic solution. To measure the adsorbed dye concentration on the nanorod/bottle brush TiO₂ electrode surface, the dye-loaded TiO₂ samples were desorbed by a 0.1 M NaOH solution in water and ethanol (50:50, v:v) for 10 min. The dimension of the TiO₂ electrode was 1 cm². The adsorbed dye was quantitatively determined from the absorbance at 510 nm measured by UV-1800, Shimadzu UV–Vis spectrophotometer. A compact and sealed dye-sensitized solar cell (DSSC) was fabricated using a standard two-electrode configuration, comprising dye-loaded Glass/FTO/P25 (with an active surface area of 0.5 cm²) as the photoanode and platinum-coated FTO as the counter electrode, which is sealed with the working electrode using a spacer (1 mm) of thermoplastic. The iodide-based electrolyte, consisting of 0.1 M lithium iodide and 0.05 M iodine in acetonitrile, was used as the redox electrolyte and injected into the inter-electrode space from the counter electrode side through a pre-drilled hole.

(d) Results and discussion

Figure 27 a, b show the FESEM micrographs of TiO_2 nanorods at different magnifications. Figure 27 a shows typical FESEM images of the TiO_2 nanorod film grown at (1:1) volume of distilled water and concentrated HCl at 180 °C for 3 h. The lower magnified image reveals that the entire surface of the FTO substrate is covered very uniformly with TiO_2 nanorods. Figure 27 b shows higher magnified FESEM image reveals 250 nm diameter of nanorods. The nanorods are tetragonal in shape with square top facets due to tetragonal rutile crystal structure. These nanorods are perpendicular to FTO substrate.

Figure 27 c shows SEM image of TiO_2 sample synthesized at 170 °C for 9 hrs. using 1:0.9 volume ratio of H_2O and concentrated HCl. The deposited samples exhibit bottle brushes of TiO_2 nanostructures containing nanorods are well covered around the entire substrate. These bottle brushes are 1.8 μm in diameter and several micrometers in length. Interestingly, the highly magnified image shows uniform distribution of tetragonal nanorods of 75 nm diameter. The diameter of the nanorods of bottle brush sample is drastically reduced up to 75 nm. The nanorods are centered at the center. The same morphology is very similar to bottle brush flower found in the environment as shown in inset of Fig 27 d. In the present investigation, we have used strong acid approach “dissolve and grow process” for the synthesis of TiO_2 nanorods and bottle brush nanostructures. It is well known that the equal volume of HCl: H_2O is beneficial for the synthesis of aligned TiO_2 nanorods [74,75]. Initially, we have adopted HCl: H_2O (1:1 v:v). The concentrated HCl constraint on the hydrolysis of the TiO_2 precursor results in 1D TiO_2 nanorods. The growth of oriented TiO_2 nanorods requires slow hydrolysis of TTIP in a fairly strong acidic aqueous medium. However, the system concentration plays a key role for completion of hydrolysis of titanium precursor. The 1:0.9 precursor ratio increase rate of hydrolysis facilitates rapid formation of nanorods that causes growth of bunch of bottle brushes.

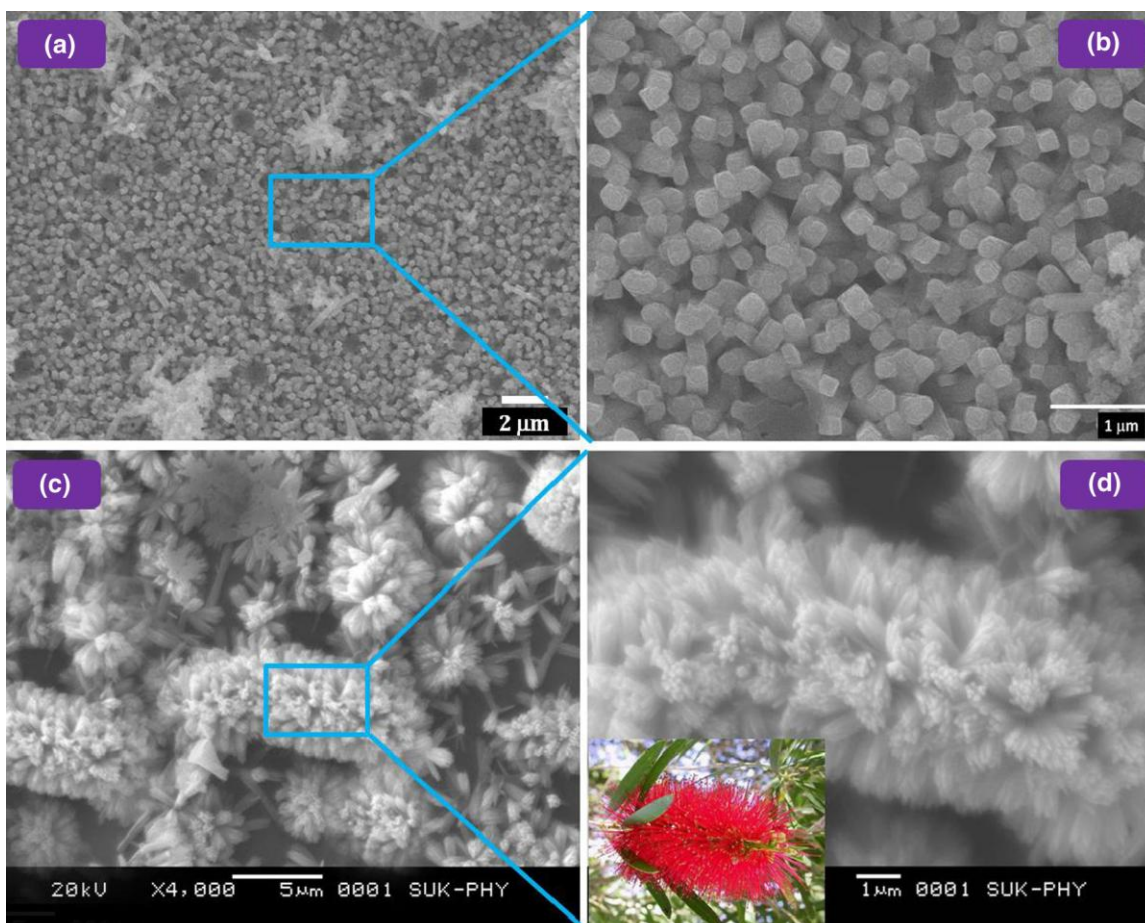


Fig. 27 (a) FESEM micrograph of hydrothermally processed TiO_2 nanorods. (b) Highly magnified FESEM image of selected area. (c, d) Bottle brush at different magnifications. Inset of d shows a photograph of natural bottle brush flower

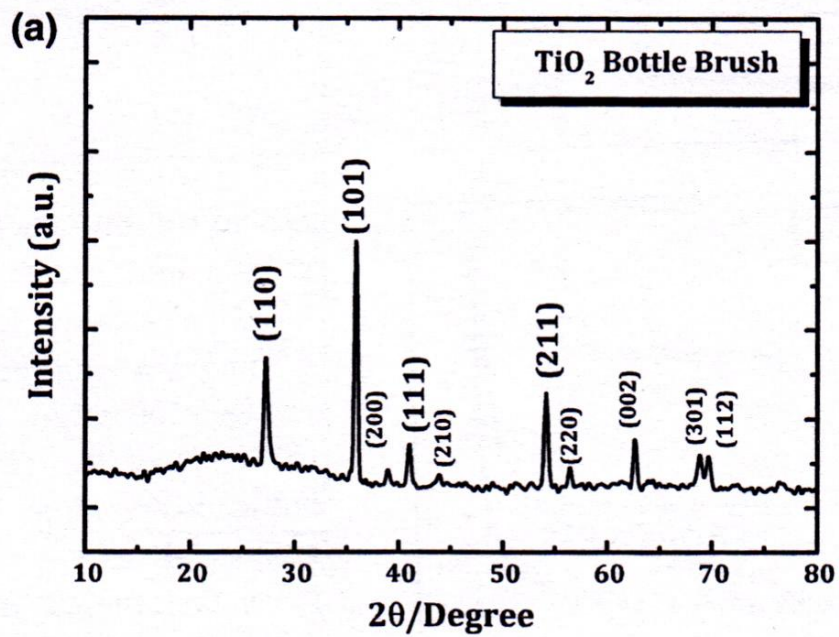


Fig. 28 : XRD pattern of synthesized TiO_2 bottle brush.

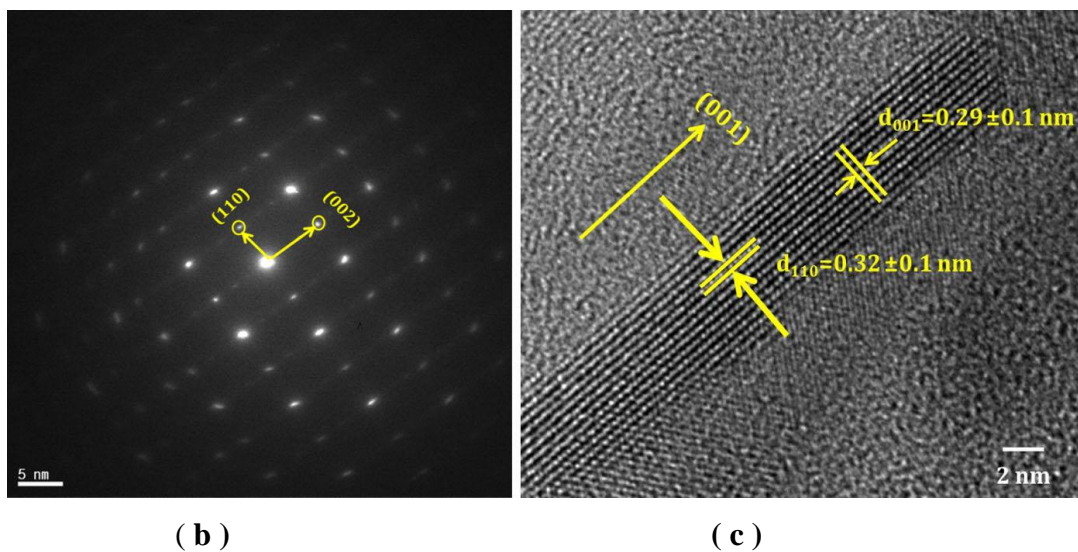


Fig. 29 : (a) Selective area electron diffraction pattern of TiO_2 bottle brush sample and (b) High-resolution transmission electron microscopic image of TiO_2 bottle brush

Figure 28 shows the XRD pattern of the TiO₂ bottle brush sample deposited on glass substrate. The comparison of “d” values in observed XRD patterns with those from the standard JCPDS data (084-1284) confirms the formation of TiO₂ phase having tetragonal rutile phase crystal structure. The lattice parameter values “a” and “c” for tetragonal structure calculated for the deposited film are found to be in good agreement with the reported values. Ten distinct reflections such as (110), (101), (200), (111), (210), (211), (220), (002), (301), and (112) are at 27.480, 36.140, 39.250, 41.310, 44.120, 54.400, 56.720, 62.870, 69.100, and 69.900, respectively, which show the tetragonal rutile phase of TiO₂. The presence of broad XRD peak is an indication of small crystallite size in the range of nanoscale, affirming the nanocrystalline nature of the TiO₂ samples. Figure 29 (a) shows the selected area electron diffraction (SAED) pattern of the TiO₂ bottle brush sample. The SAED pattern of the rutile crystal shows a spot pattern which indicates a single-crystalline nature of the rutile TiO₂ bottle brushes. The clear lattice fringe of the single nanorod of the bottle brush sample is observed to be single crystalline along their entire length. The interplanar spacing obtained from the HRTEM lattice fringes of along $d_{110} = 0.32 \pm 0.1$ nm between the adjacent lattice fringes perpendicular to the rod axis can be assigned to the rutile TiO₂ (110). The lattice spacing of $d_{001} = 0.29 \pm 0.1$ nm along the longitudinal axis direction pertains to the d-spacing of rutile TiO₂ (001) crystal planes [73, 76]. This indicates the formation of a single-crystalline rutile phase grew along [001] axis (Fig. 29 (b)).

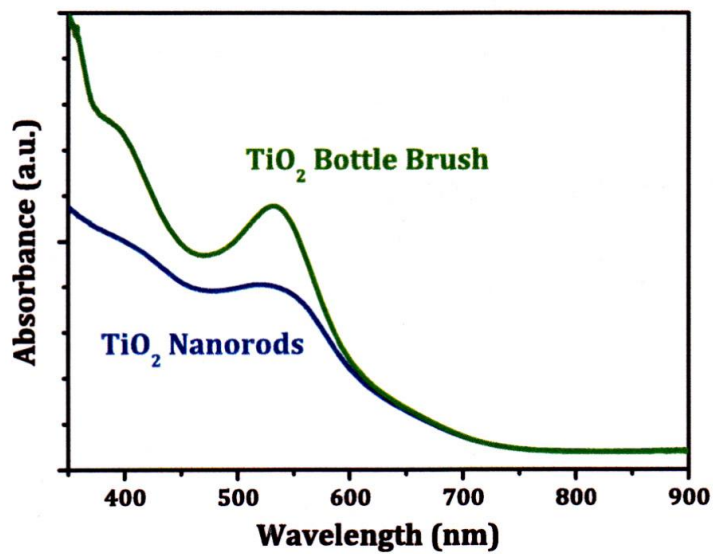


Fig. 30 : UV-Vis absorption spectra of N-719 Dye-loaded TiO_2 nanorods and bottle brush

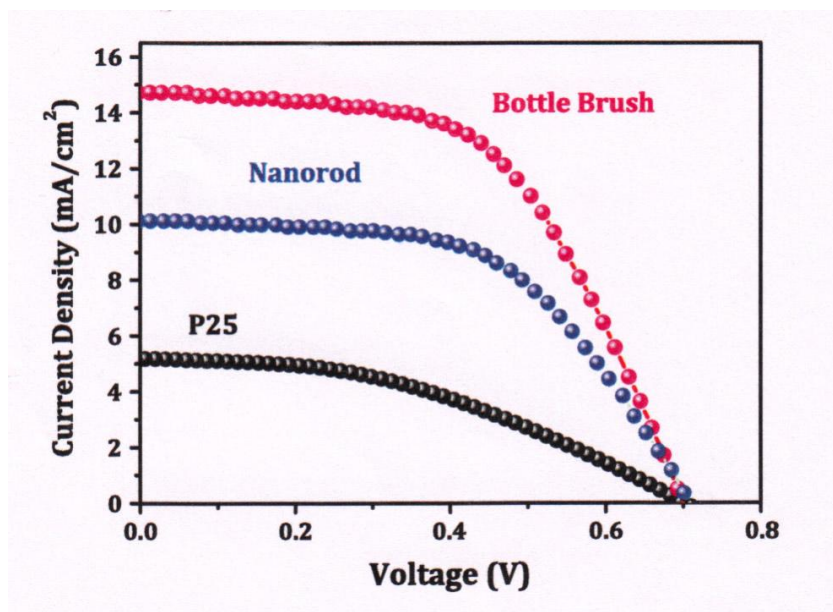


Fig. 31 : J-V curves of the DSSCs assembled from commercial P25 Degussa nanoparticles, TiO_2 nanorods, and TiO_2 bottle Brush

Figure 30 shows the absorption spectra of the dye-loaded TiO₂ nanorods and bottle brush. The absorption peaks in the range of 450–650 nm are obtained in the spectra of both TiO₂ samples. However, the intensity of the absorption peak is obviously enhanced for bottle brush sample. The dye adsorptions of these two electrodes are also observed in this work, and the amount of dye loaded on the TiO₂ bottle brush increased from 98 to 156 $\mu\text{mol}\cdot\text{cm}^{-2}$. It has been evidenced that the branches of the TiO₂ bottle brush can adsorb dye effectively than TiO₂ nanorods.

Figure 31 shows the J–V characteristics of commercial P25 Degussa, TiO₂ nanorod, and bottle brush DSSCs photoelectrodes. The TiO₂ DSSC devices assembled using the above films were tested under simulated AM1.5 Gsolar illumination (100mWcm^{-2}). The P25-based device shows $5.1\text{ mA}\cdot\text{cm}^{-2}$ short circuit current density (J_{sc}) and 0.7 V open-circuit voltage (V_{oc}) with a power conversion efficiency (η) of 1.74 % and 0.40 fill factor (FF). The DSSC based on nanorods produces 3.72 % conversion efficiency with $J_{\text{sc}} = 8.56\text{ mA}\cdot\text{cm}^{-2}$ and $V_{\text{oc}} = 0.701\text{ V}$, while the TiO₂ bottle brush produced conversion efficiency ($\eta\%$) of 6.33 % with $J_{\text{sc}} = 12.8\text{ mA}\cdot\text{cm}^{-2}$, $V_{\text{oc}} = 0.692\text{ V}$ and $\text{FF} = 0.67$.

All solar cell parameters are summarized in Table 2. Fill factors of both nanorods and bottle brush photoelectrodes show increment up to 62 and 67 %, respectively. The conversion efficiency of bottle brush sample is estimated as 6.33 %, which could be due to effective dye loading. In order to verify this, the adsorbed amounts of dye were determined by measuring the eluted dye concentration from the TiO₂ nanostructure with UV–Vis absorption spectroscopy. The P25 sample shows $88.1\text{ }\mu\text{mol cm}^{-2}$, which is less as compared to the nanorod as well as bottle brush samples. The amount of dye loaded by the nanorod sample is smaller ($98\text{ }\mu\text{mol cm}^{-2}$) compared to both bottle brush ($156\text{ }\mu\text{mol cm}^{-2}$) sample. From the above discussion, it is clear that the increment in dye absorption is simply proportional to the surface area of the TiO₂ bottle brushes. Hence 6.63% conversion efficiency for bottle brush like rutile TiO₂ film has been achieved.

Table 2 : Average photovoltaic performance parameters for DSSCs based on P25, TiO₂ nanorods and bottle brush

Sample	Voc (V)	Jsc (mA cm⁻²)	Fill factor (%)	Absorbed dye (μmol cm⁻²)	Efficiency (η) (%)
P25	0.700	5.1	40	88.1	1.74
Nanorods	0.701	8.56	62	98	3.72
Bottle brush	0.739	12.8	67	156	6.33

8. CONCLUSION

1. Different nanostructure and well crystalline rutile TiO_2 were obtained on FTO substrate by hydrothermal method.
2. From XRD data, we concluded that all the prepared TiO_2 films showed nanosize crystalline nature having crystallite size in range between 30-35 nm.
3. The deposited nanosize rutile TiO_2 thin film was confirmed by good agreement of TEM and XRD analysis.
4. FTIR spectrum confirmed the formation of TiO_2 film.
5. EDX and FESEM data indicate that, the percentage composition as well as surface morphology of TiO_2 films.
6. Cadmium sulphide (CdS) quantum dot have been prepared by SILAR method on the surface of TiO_2 .
7. Morphology and elemental analysis of CdS coated TiO_2 films were done from FESEM and EDX.
8. The conversion efficiency of CdS sensitized TiO_2 quantum dot solar cell was found to be 0.95%.
9. The dye sensitized solar cells (DSSCs) based on hierarchical rutile TiO_2 show the energy conversion efficiency of 1.98 %. After TiCl_4 aqueous solution treatment on the TiO_2 film, the energy conversion efficiency enhanced from 1.98% to 2.73%. TiCl_4 treatment improved the adhesion of the TiO_2 .
10. The DSSCs based bottle brush sample has conversion efficiency of 6.63 % compared with nanorod based DSSCs (3.72 %) due to increased surface area which is much higher than nanorods or nanoflowers. This method will open a new approach to develop hierarchical functional nanomaterials using hydrothermal process

9. SUMMARY OF THE PROJECT

The solar cells technology is not new but the kind of work undertaken by us is to fabricate low cost, higher conversion efficiency and stable solar cells. Hence our one of the objectives is to use cost-effective and low temperature method like hydrothermal technique to grow high quality TiO_2 and CdS-TiO_2 thin films for solar cells device application.

DSSCs are being developed and studied by magnetron sputtering, spray pyrolysis, e-beam evaporation and similar physical vapour deposition techniques. But if the deposition of TiO_2 is made by simple hydrothermal method, then the manufacturing cost of solar cell materials should be lower than that of materials deposited by vacuum deposition process

Nanotechnology can provide many benefits to photovoltaic (solar cell) applications by combining novel nanoscale properties with low cost. Nanorods or nanowires are interesting because they have a long axis to absorb incident sunlight. The addition of CdS to an array of nanorods improves light harvesting by adding more material to absorb incident light. These nanostructures have large area that harvest solar light and cause increased scattering that improves light absorption. It is necessary to develop simple and cost effective devices to improve power conversion efficiency of solar cells without sacrificing its long term stability.

The visible band gap semiconductor sensitization is the best option to improve power conversion efficiency. The semiconductor nanoparticles were used to protect the surface of TiO_2 , which ultimately increases the performance of the DSSCs. This approach provides an effective linkage between dye molecules and TiO_2 surface. By embedding CdS nanoparticles between the TiO_2 and dye molecules, the surface aggregation can be prevented.

The proposed work is related to the development of DSSC, based on TiO_2 and $\text{TiO}_2\text{-CdS}$ nanostructures. Once the dual sensitized devices are made stable under sunlight then efforts will be made to increase the efficiency.

Composites of TiO_2 with other in-organic materials proved to enhance power conversion efficiency. All DSSCs devices, based on CdS , CdSe , thin films were developed to improve stability of the devices. It was found that the CdS nanoparticles could improve the solar cells performance of the TiO_2 film greatly. The experimental

results indicate that the absorbance of the thin film was increased after the nanoparticle sensitization.

In the field of solar cells, one of the great strengths of TiO_2 is the ability to tailor the DSSC properties via modification of the structure. It exhibit large band gap, fast electron transportation which are useful in DSSC device technology.

Different process parameters associated with both these techniques like film thickness, precursor concentration, deposition time and temperature etc. was carefully optimized.

The thin films were characterized by using Fourier transform infra-red spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive x-ray analysis (EDS), x-ray photoelectron spectroscopy (XPS) etc. techniques. Photo-electrochemical applications were studied by using current-voltage (I-V), Incident photo-to-current conversion efficiency (IPCE).

To deposit CdS quantum dots on TiO_2 nanoflowers, we use the simple SILAR sensitization process. We described the light harvesting ability of TiO_2 nanoflowers coated with quantum dots. Cadmium sulphide quantum dot is a promising solution for low cost, high efficiency photovoltaics. The energy conversion efficiency for CdS quantum dots on TiO_2 nanoflowers is about 0.95% .

The TiCl_4 treatment on TiO_2 films enhanced the performance of resulting DSSCs. TiO_2 nanoflower films sensitized with N719 dye enhanced the power conversion efficiency from 1.98% to 2.73 %.

We have deposited bottle brush-like nanostructured TiO_2 thin films by simple and cost effective hydrothermal route. The bottle brush samples containing nanorods were 75 nm in diameter providing excellent surface area about $89.34 \text{ m}^2 \text{ g}^{-1}$, which is much higher than 1D TiO_2 nanorods $63.7 \text{ m}^2 \text{ g}^{-1}$. The synthesized nanorods and bottle brushes were successfully used for DSSCs application. Bottle brush sample has strong light-harvesting capability. Also, the bottle brush containing nanorods would provide excellent electron percolation pathways for charge transfer. As a result, the bottle brush DSSC sample has conversion efficiency of 6.63 %.

HIGHLIGHTS, ACHIEVEMENTS AND CONTRIBUTION TO SOCIETY

Renewable energy is the energy which comes from natural resources such as sunlight, wind, rain, tides, geothermal heat etc. The advantages of the renewable energy are as follows.

- 1) It is renewable therefore it is sustainable and so will never run out.
- 2) Require less maintenance than traditional generators.
- 3) The fuel, being derived from natural and available resources, reduces the costs of operation.
- 4) It produces little or no waste products such as carbon dioxide or other chemical pollutants, so Dye sensitized solar cells are Environmental friendly.
- 5) Although the present work is primarily experimental, multiscale thinking can provide valuable direction for the quantum dot solar cell and DSSCs.
- 6) Industrially important solar cell due to its low cost.
- 7) These results may be useful for further progress in the field of solar cells (photovoltaic devices). The kind of work undertaken by us is to fabricate low cost, high conversion efficiency and stable solar cells by using simple and low temperature hydrothermal method. By using such a cost effective method we got the conversion efficiency of 6.63% in case of bottle brush like rutile TiO_2 thin film.

Thus the project is successfully completed.

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11. INTERNATIONAL PUBLICATIONS / PRESENTATIONS RESULTING FROM THE WORK

- 1) Hydrothermal synthesis of rutile TiO₂ bottle brush for efficient dye-sensitized solar cells
Journal of nanoparticle research 16 – 6 (2014) 1 – 11
- 2) Characterization of TiO₂ thin films deposited by hydrothermal method.
2nd International Conference on “Physics of Materials and Materials Based Device Fabrication – (ICPM-MDF-2014)” 13th –15th January 2014
Department of Physics, Shivaji University, Kolhapur, Maharashtra.
- 3) Synthesis and characterization of hydrothermally grown CdS Sensitized TiO₂ for quantum dot solar cells.
International Photovoltaic Solar Energy Conference (IPSEC) SOLAR ASIA - 2015
30th July – 1st August, 2015, Department of Physics Savitribai Phule Pune University, pune, Maharashtra.
- 4) Synthesis and Characterization of TiO₂ thin films on FTO by hydrothermal process.
Raman Memorial Conference (2015) 13th –14th February 2015
Department of Physics, Savitribai Phule Pune University, Pune, Maharashtra.
- 5) One paper entitled ‘Nanocrystalline Flowers of Rutile TiO₂ Synthesized By Hydrothermal Method’ is submitted to journal named “Bulletin of Materials Science” (manuscript Draft is attached at the end of the report)
Thus the project is successfully completed.



Bharati Vidyapeeth Deemed University, Pune (India)

(U/s 3 of UGC Act, 1956 Vide Notification No. F.9-15/95-U.3 of the Govt. of India)

Hon'ble Dr. Patangrao Kadam

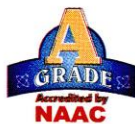
M.A., LL.B., Ph.D.

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Prof. Dr. Shivajirao Kadam

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REACCREDITED WITH 'A' GRADE BY NAAC

Ref.No.BVDU/Ph.D./2013-2014/ **2541**

22 October 2013

LETTER OF PROVISIONAL ADMISSION

To,
Mr. Sudhir Vavale
At Post Bhare Tal :- Mulashi,
Dist :- Pune.- 412115.

Sub: Admission for Ph.D.-2013-14

Sir/Madam,

I am directed to inform you that the authorities of Bharati Vidyapeeth Deemed University have been pleased to grant you provisional admission for the Ph. D. degree course in **Physics** under the faculty of **Science** with effect from **16th September, 2013** Subject to the fulfillment of the eligibility and other conditions.

Name of your Research guide, place of Research and payment of fees shall be as shown below.

- | | |
|------------------------------|--|
| 1.Name of the Guide | - Dr.H.P.Deshmukh |
| 2.Place of Research | - Yashwantrao Mohite College of Arts, Science and Commerce,Paud Road, Erandwane,Pune |
| 3. Fees- (First year) | a) Tuition Fee Rs. 30,000/-
b) Eligibility Fee Rs. 500/- |

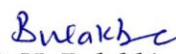
Fees will be paid in the office of University by cash or Demand draft in the name of "The Registrar, Bharati Vidyapeeth Deemed University, Pune."

You will have to submit the application for the registration of the degree of Doctor of Philosophy (Ph.D) along with the following documents through your guide and Head of the Institution to the University.

- 1) An authenticated copy of statement of marks and degree certificates (Graduate, Post –graduate degree.)
 - 2) Migration / Transference certificate.
 - 3) Cast validity certificate (if applicable)
 - 4) No Objection Certificate (NOC) from the employer, if the candidate is employed else where
 - 5) Fee receipts
 - 6) Five copies of Plan of Research work
 - 7) * Copy of passport
 - 8) * Research visa
 - 9) * Residential permit
- (* applicable to international students / NRI/ PIO)

Please note that your final registration for the Ph.D.degree programme will be subject to satisfactory completion of Pre Ph.D. course work, and such other conditions as may be prescribed time to time.

Yours faithfully,


(**Dr. P. M. Bulakh**)
Director, BCUD

Copy forwarded with compliments to

- 1.Principal, Yashwantrao Mohite College of Arts, Science and Commerce, Paud Road, Erandwane, Pune
2. Dr.H.P.Deshmukh, Research guide. Yashwantrao Mohite College of Arts, Science and Commerce, Paud Road, Erandwane, Pune

2nd International Conference on
"Physics of Materials and Materials
Based Device Fabrication (ICPM-MDF-2014)"



Organized by
Department of Physics, Shivaji University, Kolhapur
(UGC-DRS-I, DRS-II, ASIST, DSA-I, DST-FIST I & II, DST-PURSE SPONSORED DEPARTMENT)
(Jan 13-15, 2014)

CERTIFICATE

This is to certify that Prof./Dr./Mr./Ms. *Deshmukh H. P.*
of *Bharati Vidyapeeth's University, Pune.* has participated actively, ☐ worked
as resource person ☐ chaired the session ☒ presented poster ☒ worked as local organizing committee member ☐ in the
2nd International Conference on Physics of Materials and Materials Based Device Fabrication (ICPM-MDF-2014) held at Department of
Physics, Shivaji University, Kolhapur (M.S.), India during January 13-15, 2014. His/Her contribution to the conference is highly
appreciated.


Prof. (Dr.) C. D. Lokhande
Convener, ICPM-MDF-2014,
Head, Dept. of Physics


Prof. (Dr.) C. H. Bhosale
Chairman,
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INTERNATIONAL PHOTOVOLTAIC SOLAR ENERGY CONFERENCE (IPSEC)



(SOLAR ASIA - 2015)

30th JULY – 1st AUGUST, 2015

Organized by

**Department of Physics
Savitribai Phule Pune University
(formerly University of Pune)
Pune- 411 007, INDIA**

CERTIFICATE OF APPRECIATION

This is to certify that Prof./Dr./Mr./Ms. Sudhis D. Vavale
.....from Y.M. College Bharati Vidyapeeth Pune has
delivered a plenary talk/invited talk/participated and presented a
paper (Oral/Poster/Thesis) entitled "Synthesis and Characterization
of hydrothermally grown TiO₂ Sensitized with CdS for
SSC" in the
International Photovoltaic Solar Energy Conference, SOLAR ASIA -2015.

Sone

**Dr. N. B. Chaure
Convener
IPSEC-2015**

Patil

**Prof. S. I. Patil
Chairperson
IPSEC-2015**

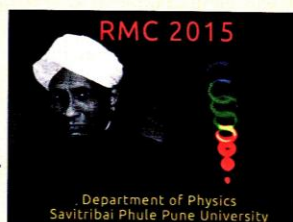
Dharmadasa

**Prof. I. M. Dharmadasa
Initiating member of
SOLAR ASIA**

RAMAN MEMORIAL CONFERENCE 2015

Certificate of Participation

This is to certify that *Sudhir Vavale*
made an oral presentation at / presented a poster at /
attended the Raman Memorial Conference held on
13th & 14th February 2015 at the Department of
Physics, Savitribai Phule Pune University, Pune.



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RMC 2015

S. Patil
Head - Department of Physics
Savitribai Phule Pune University

Synthesis and characterization of hydrothermally grown TiO_2 sensitized with CdS for quantum dot sensitized solar cells.

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TiO_2 thin film was synthesized on a transparent conductive fluorine-doped tin oxide substrate by a hydrothermal method. The formation of CdS quantum dots layer on TiO_2 film were carried out by a chemical bath deposition (CBD) method. The structural and morphological properties of the samples were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The results indicate that CdS QDs are uniformly coated on the surface of the TiO_2 film. The shift of light absorption edge was carried out by taking UV-visible absorption spectra. Compared with the absorption spectra of the TiO_2 film deposition of CdS QDs shifts the absorption edge to the higher wavelength. The enhanced light absorption in the visible-light region of CdS/ TiO_2 film indicates that CdS layers can act as sensitizers in quantum dots sensitized solar cells (QDSSCs).

Keywords: - Thin film, Hydrothermal, quantum dot, XRD, FESEM.

Synthesis and Characterization of TiO_2 thin films on FTO by hydrothermal process

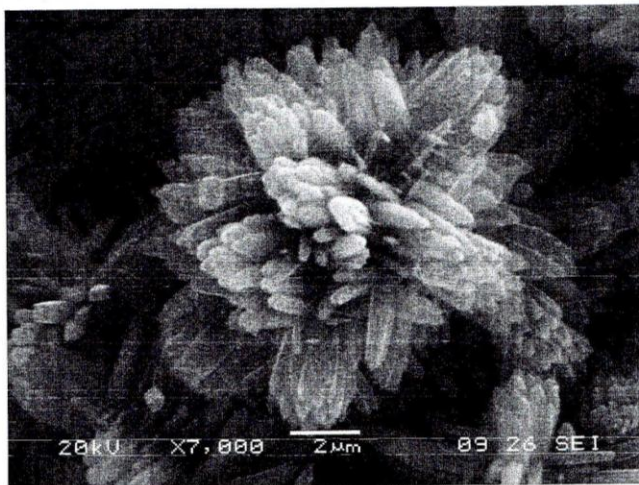
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Abstract:

TiO_2 thin films were deposited on the fluorine doped tin oxide (FTO) via hydrothermal technique using tetra butyl titanate as precursor. To prepare the TiO_2 thin films on FTO, the co-surface treatment was given by immersing the TiO_2 films in TiCl_4 aqueous solution. The structural, morphological and optical properties of synthesized TiO_2 thin films were investigated using X-ray Diffraction, Scanning Electron Microscopy, and UV-Vis spectral techniques. The XRD results showed the formation of polycrystalline TiO_2 having rutile phase. The SEM images reveals well growth of TiO_2 crystallites in form of micro-flower having nano-petals. The optical absorption spectra of TiO_2 films over the FTO surface showed well visible light absorption in wavelength range 300nm to 800nm.



Hydrothermal synthesis of rutile TiO₂ bottle brush for efficient dye-sensitized solar cells

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H. P. Deshamukh · Chang Su Shim ·
Pramod S. Patil · Chang Kook Hong

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Abstract Hydrothermal process has been employed to synthesize titanium oxide (TiO₂) bottle brush. The nanostructured bottle brushes with tetragonal nanorods of ~75 nm diameter have been synthesized by changing the nature of the precursors and hydrothermal processing parameters. The morphological features and structural properties of TiO₂ films were investigated by field emission scanning electron microscopy, X-ray diffraction, high-resolution transmission electron spectroscopy, Fourier transform Raman spectroscopy, and X-ray photoelectron spectroscopy. The influence of such nanostructures on the performance of dye-sensitized solar cells (DSSCs) is investigated in detail. The interface and transient properties of these nanorods and bottle brush-based photoanodes in DSSCs were analyzed by electrochemical impedance spectroscopic measurements in order to understand the critical factors contributing to such high power conversion efficiency. Surface area of sample was recorded using Brunauer–Emmett–Teller measurements. It is found that bottle brush provides

effective large surface area 89.34 m² g⁻¹ which is much higher than TiO₂ nanorods 63.7 m² g⁻¹. Such effective surface area can facilitate the effective light harvesting, and hence improves the dye adsorption and the photovoltaic performance of DSSCs, typically in short-circuit photocurrent and power conversion efficiency. A best power conversion efficiency of 6.63 % has been achieved. We believe that the present device performance would have wide interests in dye-sensitized solar cell research.

Keywords Hydrothermally processed TiO₂ bottle brush · Raman · 6.63 % solar conversion efficiency · Energy

Introduction

Nanowires/nanorods have demonstrated a great potential to achieve high diffusion coefficient of carriers in electric devices due to their unique one-dimensional (1D) structure (Law et al. 2005). Many attempts have been made for controlling the 1D nanostructured TiO₂ using different techniques which include electrodeposition (Kang et al. 2007), hydrothermal and solvothermal (Kasuga et al. 1995; Mali et al. 2011; Kumar et al. 2011; Liu and Aydil 2009; Sun et al. 2012, 2013), anodization (Gong et al. 2001), template-based growth sol-gel electrophoresis (Ren et al. 2009), and by

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Final Report Assessment/ Evaluation Certificate

(Two Members Expert Committee Not Belonging to the Institute of Principal Investigator)

It is certified that the final report of Major Research Project entitled "Dual Sensitization of Hydrothermally grown TiO_2 for Efficient Solar Cells" by Dr. H. P. Deshmukh, Assistant Professor, Department of Physics, Yashwantrao Mohite College of Arts, Science and Commerce, Bharati Vidyapeeth (Deemed to be University), Erandwane, Pune, Maharashtra has been assessed by the committee consisting the following members for final submission of the report to the UGC, New Delhi under the scheme of Major Research Project.

Comments/Suggestions of the Expert Committee:-

1. The TiO_2 and CdS-TiO_2 thin films are fabricated for the solar cell applications. The method used for deposition of TiO_2 thin films is hydrothermal method which is simple and cost-effective. The addition of CdS to an array of nanorods improves light harvesting by adding more materials to absorb incident light.
2. The quantum dot sensitized solar cells (QSS) and dye-sensitized solar cells (DSSCs) are prepared and tested for the efficiency. It is found that DSSCs performance is the best. The work is published in Scopus-indexed Journal named "Journal of Nanoparticle Research" as well as 3 international conferences which is the great achievement and indicates quality of Research.

Name & Signatures of Experts with Date:-

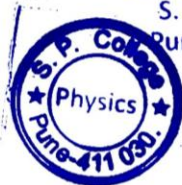
1. Dr. H. K. Waghelkar

2. S. B. Jagtap

Name of Expert

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05/10/2023