

INVESTIGATION OF PHYSICAL PROPERTIES OF MESOPOROUS NANO-TiO₂ FOR DYE-SOLAR CELLS APPLICATIONS

GUGU HLENGIWE MHLONGO

Thesis presented in fulfillment of the requirements for the degree of Master of
Sciences at the University of Zululand.

Supervisor: Prof. M. Maaza

Nano-Science Laboratory, MRG, Ithemba LABS

Co-supervisor: Prof. O.M. Ndwandwe

Dept. of Physics and Engineering, University of Zululand

2008

Acknowledgments

First and foremost, I would like to thank Father in Heaven, for all His support and guidance during these years. I am grateful to my supervisor, Dr Maaza whose brilliant academic guidance and encouragement, time, patience, enthusiasm and support made this work meaningful and a success. I would also like to express my sincere appreciation and thanks to Prof Ndwandwe for giving me the opportunity of being part of the Manus/Matsci program. To late Dr Terence Marais, for his warm welcome and support in Cape Town.

I would like to extend my deep appreciation to:

- To all iThemba LABS -Material Research Group «MRG» staff
- Chris and Sotobe, guys it was great sharing an office with you
- Dr Chris Theron, for welcoming us at MRG, for his constant support and his input on making my visit to Japan and Taiwan successful.
- South African government-National Research Foundation «NRF» for funding my project
- University of Zululand and University of the Western Cape for academic support.

Great thanks to Professor Alain GIBAUD from the University of Le Mans in France and the French Centre national pour la Recherche Scientifique for his help and the samples synthesized by the method developed in his laboratory.

Millions of thanks to Dr Hajime HANEDA of National Institute for Material Science (NIMS) in Tsukuba Japan, for his warm welcome in Japan and for giving me the

opportunity of using different techniques: Grazing Incidence XRD, AFM, HRSEM, UV-VIS-NIR, PL.

I will send a special thank to my family for their support towards my success. I cannot forget to mention my parents Mrs. Fikile Mhlongo and Mr. Mkhanyiseni Mhlongo for their love, patience, support, and understanding all these years. Most of all I would like to thank them for taking care of my lovely daughter Londeka while I was still busy with my studies.

Finally, I'm grateful to S'bongiseni Ndimande for his love, patience and for being always there for me and our daughter Londeka Ndimande.

Abstract

The nanocrystalline dye sensitized solar cells, so called «Grätzel cells» are based on a wide band gap «3.0-3.2eV» semiconductor TiO_2 in its nano-scaled form. These nano-sized TiO_2 are sensitized by a dye monolayer so to increase its spectral response and are immersed in a redox electrolyte for charge transfer. At the present moment, the best overall sunlight to electrical energy conversion efficiency under direct and diffuse sunlight laboratory devices is about 7-11%. It is well acknowledged in the literature that the low efficiency of standard large dimension Grätzel solar cell which varies in the range of 2-5% is caused by the excitonic fast recombination. In order to improve this conversion efficiency and reach values comparable with standard PV technologies, it is necessary to minimize this charge recombination at TiO_2 -dye interface in addition to an optimized optical path management. The conversion efficiency is related to the Incident Photon-Current Efficiency «IPCE» via the charge carrier free mean path «L» and the absorption coefficient α of the dye- TiO_2 system.

$$\text{IPCE} = \frac{1}{1 + \frac{1}{\alpha L}}$$

Where L is related to charge carrier lifetime « ζ » and its diffusion constant «D» and mobility « μ »:

$$L = \sqrt{D\tau} \quad , \quad D = k_B T \frac{\mu}{e}$$

Hence nano- TiO_2 with substantial shape anisotropy such as TiO_2 nanorods/nanotubes or 1-D porous TiO_2 structures would exhibit less interfacial scattering as a result of a larger lifetime and efficient light trapping. This trapping effect would offer a better electron transport in the nano- TiO_2 electrodes as a result of faster photoresponse and higher electron collection efficiency. This research project focuses

mainly on engineering meso-porous 1-D type TiO_2 nano-structures with an obvious shape anisotropy for possible application in DSCs application which is expected to minimize the fast electron/hole pair recombination process. In this work we report the high-density arrays of mesoporous anatase TiO_2 nano-structures derived using the combination of Evaporation Induced Self-Assembly (EISA) and sol-gel methods using Pluronic P123 « EO_{23} - PO_{70} - EO_{23} » as a surfactant and Titanium isopropoxide « $\text{Ti-O}^i\text{Pr}_4$ » as a starting material . The mesoporous TiO_2 films were prepared by dip coating method using ITO coated float glass as a substrate.

The phase and crystallinity information was determined from small angle grazing incident-XRD. The average crystallite size of the TiO_2 nanoparticles was estimated using Scherer's equation. X-ray reflectivity (XRR) and grazing incidence small angle x-ray scattering were used to follow the order and disorder in the formation of the mesoporous nano-structured TiO_2 and also to track the evolution of the films structure before and after calcinations. Optical analyses were done using UV-VIS-NIR spectroscope. The Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) were used to observe the surface morphology and surface roughness of the mesoporous TiO_2 nanostructures, respectively. Elemental analyses were done using X-Ray Photoelectron Spectroscopy (XPS). Photoluminescence (PL) measurements were done using an Argon laser source at an excitation wavelength of 476 nm in order to study the defects present in the samples.

List of acronyms

DSCs	Dye-sensitized Solar Cells
PV	Photovoltaic
CIS	Copper Indium Selenide
Pluronic 123	$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_{70}(\text{CH}_2\text{CH}_2\text{O})\text{H}_{20}$
Ti-O ⁱ Pr ₄	Titanium Isopropoxide
UV-VIS-NIR	Ultraviolet Visible Near-Infrared
XRD	X-Ray Diffraction
PL	Photoluminescence
AFM	Atomic Force Microscopy
IPCE	Incident Photon-Current Efficiency
TiO ₂	Titanium Dioxide
SnO ₂	Tin Dioxide
ZnO	Zinc Oxide
TCO	Transparent Conduction Oxide
ITO	Indium Tin Oxide
FTO	Fluorine Tin Oxide
Nb ₂ O ₅	Niobium (V) Oxide
SrTiO ₃	Strontium Titanate
Ru	Ruthenium
N-3	cis-RuL ₂ -(NCS) ₂ , where L stands for 2, 2'-bipyridyl-4, 4'-dicarboxylic acid
N-719	cis-di (thiocyanato)-N, N'-bis (2, 2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) Ruthenium (II)
Z-955	cis-Ru (dppbpy) (dnbpy) (NCS) ₂ (dppbpy= 4, 4'-diphosphonic acid-2, 2'-bipyridine; dnbpy = 4, 4' dinonyl-2, 2'-bipyridine)

Ru-535	cis-bis (4,4'-dicarboxy-2,2'-bipyridine)-bis (isothiocyanato) Ruthenium(II)
K-77	Ru (2,2'-bipyridine-4,4'-dicarboxylic acid) (4,4'-bis (2-(tert-butylloxyphenyl) ethenyl)-2,2'-bipyridine) (NCS) ₂
Fe-based dye	cis-[Fe ¹¹ (2, 2-bipyridine-4, 4'-dicarboxylic acid) ₂ (CN) ₂]
NREL	National Renewable Energy Laboratory, Midwest Research Inst.
OSU	The Ohio State University, Dept. of Chemistry
AIST	National Inst. for Advanced Industrial Science and Technology, Japan
IAE	Institute of Advanced Energy, Kyoto University, Japan
EPFL	Laboratory for photonics and Interfaces, Swiss Federal Institute of Technology, Switzerland
MRL	Material Research Laboratory, the Pennsylvania State Univ.
LNES	Laboratorio de Nanotecnologia e Energia Solar, Instituto de Quimica
ECN	Solar and Wind Energy, Netherlands
IPP	Institute of Plasma Physics, Division of Solar Energy Materials and Engineering, the Hefei University of Technology
NIMC	National Institute of Materials and Chemical Research, Tsukuba, Japan
CEA	Le Ripault, Département Matériaux, France
EISA	Evaporation Induced Self Assembly process or
KLE	poly (ethylene-co-butylene)-block-poly (ethylene oxide)
TG	Thermogravimetric
XRR	X-Ray Reflectrometry
GI-SAXS	Grazing Incident-Small Angle X-ray scattering
GI-XRD	Grazing Incident-X-Ray Diffraction

List of symbols

μ	drift mobility
α	absorption coefficient
ζ	charge carrier lifetime
L	free mean path
T	temperature
e	electron charge
D	diffusion constant
$\Delta\Phi_{sc}$	potential drop
k	Boltzmann constant
N_D	dopant concentration
W	space charge layer
ϵ	dielectric constant
ϵ_0	permittivity
r	distance
r_0	initial distance
L_D	Debye length
U	constant coating speed
ρ	density
D	strain rate tensor
η	shear stress
c_p	specific heat
λ	thermal conductivity or wavelength
L	velocity gradient
u_s	velocity of the surface
u_v	velocity of the vapor

n	unit orientation of the interface
P	pressure
p_v	vapor pressure
Π	disjoining pressure
ρ_v	mass density
K	curvature of the film surface
grad_s	gradient of the film surface
A	Hamaker constant
L	latent heat of evaporation
T_s	film surface temperature
T_v	vapour temperature
J_T	standard value
U	constant coating speed
T_0	constant temperature
j_0	evaporation rate
P	reference pressure
C	Capillary number
C^*	Effective capillary number
A^*	Van der Waals number
V^*	Vapor recoil number
G^*	Gravity number
M^*	Marangoni number
E^*	Evaporation number
s	equilibrium surface tension
β	width
n	refractive index
d	film distance

Table of contents

CHAPTER 1	1
1. INTRODUCTION	1
1.1 Objective and scope of the dissertation	11
1.2 Dissertation layout	14
CHAPTER 2	15
2. DYE-SENSITIZED SOLAR CELLS	15
2.1 Natural photosynthesis	15
2.1.1 Artificial photosynthesis and principle of the DSCs technology.	19
2.2 Porous nano-structured semi-conducting electrode.....	26
2.3 Absorbing dye complex	27
2.4 Electrolyte and counter electrode.....	33
2.5 DSC standard assembling process and costs related	36
CHAPTER 3	38
3. TiO₂ PROPERTIES	38
3.1 Key properties of bulk TiO₂	38
3.2 Redox power of semiconductors and choice of TiO₂	40
3.3 Structural and crystallographic properties of TiO₂	42
3.4 Electronic properties of TiO₂ and size effects.....	47

CHAPTER 4	58
4. LITURATURE REVIEW	58
4.1 Evaporation induced self assembly (EISA).....	58
4.1.1 Evaporation induced self assembly (EISA) of mesoporous TiO ₂ : survey. ...	64
4.1.2 Experimental observations of the induced ordering during the EISA of mesoporous TiO ₂	69
4.1.3 Modeling of the rheology change during the EISA process.....	76
CHAPTER 5	84
5. EXPERIMENTAL.....	84
5.1 Synthesis of mesoporous TiO₂ nanostructures	84
5.2 Results and discussion	86
5.2.1 Structural ordering and surface morphology.....	86
5.2.2 Crystallography and texturing properties	91
5.2.3 Optical and band-gap properties.....	95
5.2.4 Defects and photoluminescence properties.....	101
5.2.5 Bonding chemical and electronic properties	105
Summary and conclusion	108
References	110

List of figures

Figure 1: The solar conversion can take place from both DSC cell's faces.	4
Figure 2: Variation of cost with efficiency in regions I, II, and III.	5
Figure 3: The world solar energy map illustrating annual average solar irradiances across the world.....	7
Figure 4: Response time vs. open circuit voltage for nano-particles and nano-tubes [Bro-2006].	9
Figure 5: Schematic diagram showing the electron transport across (a) random oriented spherical TiO ₂ nanoparticles, (b) ordered TiO ₂ nanoporous arrays and (c) meso-porous nano-TiO ₂	10
Figure 6: Dynamic competition between the transport of the photo-generated electrons and their interfacial recombination.....	13
Figure 7: Photosynthesis mechanisms in plants	17
Figure 8: Molecular configuration of the natural chlorophylls and their respective optical Absorption spectra [Liz-2004].....	18
Figure 9: Schematic representation of DSCs.....	21
Figure 10: IPCE curves illustrating the rate of conversion in (a) bulk TiO ₂ and (b) nano-crystalline TiO ₂ based solar cells.....	22
Figure 11: Charge creation and charge separation in (a) standard PV Si based and (b) a typical dye solar cell	25
Figure 12: (a) The molecular structure of the dyes N3, Black dye and N719 used in the EPFL Gratzel initial cells. (b) Spectral response «incident photon to current conversion efficiency» curve of dye-sensitized solar cell for difference dyes compared with the spectral response of pure TiO ₂ electrode [Hal-2002, Tol-2003, Gre-2004].....	28

Figure 13: Importance of binding states between photosensitizing molecules and the TiO_2 surface for efficiency in a dye-sensitized [Mur-1995].	32
Figure 14: Operation of counter electrode in DSCs.	34
Figure 15: Photocurrent-voltage characteristics of nc-DSC [Mur-1995].	37
Figure 16: Energy-level diagram for various semiconductors indicating the energy.	41
Figure 17: Different crystalline forms of bulk TiO_2 : (a) anatase, (b) rutile and (c) brookite.	45
Figure 18: Diagram indicating the difference of band bending at semiconductor solution interface between n-type bulk semiconductor and nanoparticle semiconductor.	50
Figure 19: Density functional theory optimized geometry of the Ru-polypyridyl dye N3 on a TiO_2 nanocrystal [Per-2002].	53
Figure 20: Atomic sites of Ti and O in the elementary cell of (a) rutile and (b) anatase phases.	56
Figure 21: Face (001) of the rutile phase; projections on the 001 plan [Per-2002].	57
Figure 22: Four major steps that occur during evaporation induced self assembly.	60
Figure 23: the isotropic, cubic, 2-D hexagonal and lamellar configurations depend on the temperature-surfactant concentration phase diagram.	62
Figure 24: typical structures of mesoporous (a) WO_3 , (b) CeO_2 , (c) TiO_2 (d) ZrO_2 and (e) ITO synthesized by using the KLE family as block co-polymers and the standard Brij58 [Bre-2006].	63
Figure 25: Representation of the in-situ time resolved study of the TiO_2 based film formation during dip coating as revealed by simultaneous small angle x-ray scattering measurements [Son-2008].	71
Figure 26: Formation 2-D hexagonal TiO_2 mesostructure	73

Figure 27: Typical 2-D diffraction patterns corresponding to various types of mesostructures together with corresponding TEM images [Gro-2004]. ...	75
Figure 28: Schematic representation where the flat substrate moves with a constant velocity U with a predicted constant steady state film thickness h_0	83
Figure 29: SEM (a, b) and AFM (c, d) images of the mesoporous TiO_2 films after calcination.	87
Figure 30: Typical grazing incidence small angle X-ray scattering (GI-SAS)-(a) and X-ray reflectivity profile of the investigated meso-porous TiO_2 films-(b). ...	90
Figure 31: Room temperature grazing incidence XRD patterns of different mesoporous nano-structured TiO_2 films after calcination.	93
Figure 32: Room temperature UV-VIS-NIR normal incidence (a)optical transmission and (b) diffuse scattering spectra of the different meso-porous nanostructured TiO_2 films samples after calcination.	99
Figure 33: Wavelength cut-off of the different meso-porous nanostructured TiO_2 films samples after calcination.	100
Figure 34: Room temperature photoluminescence spectra of the different TiO_2 meso-porous nanostructures; Excitation laser wavelength $\lambda = 476 \text{ nm}$	104
Figure 35: Typical X-rays photoelectron spectroscopy spectra of one of the TiO_2 meso-porous nanostructure ($\text{TiO}_2\text{-A}$).	107

List of tables

Table 1: Most currently studied dyes for nanostructured solar cells..... 29

Table 2: Crystallographic properties of TiO₂ phases 46

Table 3: Atoms locations in the unit cell. 46

Table 4: Average crystallite size estimation using Scherer’s equation.....96

Table 5: Optical data for samples TiO₂-A, TiO₂-B, TiO₂-B DIL.....98

Table 6:Cut-off wavelengths of different meso-porous nanostructured TiO₂ films
samples after calcination.....98

CHAPTER 1

1. INTRODUCTION

Within the current global energy emergency, renewable energies in general and solar photo-converted electricity option specifically, are presently a growing worldwide alternative even if it was a relatively expensive energy technology. In this solar energy sector, to date, the photovoltaics «PV» have been dominated by solid-state junction devices, usually by silicon «Si» crystalline or amorphous and semiconductors based compounds such as Copper Indium Selenide, the so called CIS technology. This PV technology has taken advantage from the technology point of view and materials' availability resulting from the Si based semiconductor industry. However, recently, there is an increasing awareness of the promising advantages of devices based on mesoscopic inorganic or organic semiconductors. These are formed from nano-crystalline inorganic oxides, ionic liquids and organic hole conductor or conducting polymer based devices. They offer the prospect of low cost fabrication, not being energy intensive and/or do not require high temperature processing or/and high vacuum processing. Likewise, they exhibit a satisfactory compatibility with flexible substrates and a variety of presentations and appearances to facilitate market entry.

From cost viewpoint, it has been shown that it is possible to depart completely from the classical PV solid-state cells, which are replaced by devices based on interpenetrating network nano-junctions. The presence of a bulk junction having an interface with a significant surface-area, intrinsic to nano-compounds, endows these systems with intriguing optoelectronic properties. The corresponding devices based on interpenetrating networks of nanoscopic semiconductors have shown significant photo-conversion efficiencies taking into account the time framework during which

this novel class of solar energy devices emerged. This novel technology could compete with those of conventional devices in terms of cost effectiveness and reasonable processing/manufacturing possibilities in the South-South regions in particular. One of the prototypes of this novel class of solar energy photo-conversion is the so called Dye Solar Cells technology «DSC» or Gratzel solar cells technology. This novel molecular photovoltaic nano-materials based technology is being developed worldwide. In Gratzel solar cell the photosensitization of a large band gap semiconductor, such as nano-crystalline titania «TiO₂», is performed by an organic dye and a hole transport material which ensures that after photoexcitation and injection of electron into the conduction band of the semiconductor, the charge separation can be used directly as a photo-current as depicted in Figure 1.a. The DSC technology which is rather emerging and relatively inexpensive could be an alternative to silicon based cells due to its low production cost, respectable conversion efficiency and high potential for use in both rural and urban regions where grid network is difficult to be implemented. Even if the current maximum rate of conversion is about 11% which relatively low compared to established Si and CIS technologies [Figure 1.b], however the efficiency of this type of solar cell in low light situations remains as high as under full sun light. The research interest on this type of solar cell grew rapidly after a remarkable energy conversion efficiency of about 10-11% by Grätzel's team at the Ecole Polytechnique Federale of Lausanne (EPFL) in Switzerland [Mic-2005, Qin-2006, Dia-2007]. This substantial conversion efficiency of about 10-11% has been obtained with liquid electrolytes and artificial dyes in a laboratory scale device. However, the presence of liquid electrolyte in this device is reported to result in less long-term stability and practical limitations of sealing and leakage. Grätzel cells have many advantages over conventional silicon solar cells but the energy conversion efficiency has not yet reached the level of silicon based solar cells at the industrial scale as shown by Figure 1.b. The previously 10-11% record

conversion DSC cell is a laboratory prototype. This DSC approach; a technology located within the range of 2nd-3rd generations solar cell technologies [Figure 2] has numerous competitive edges in that it is transparent & can be developed in various colors. In contrast to the silicon «Si» and Copper Indium Selenide «CIS» based solar cells, the nano-TiO₂ based DSCs have the following intrinsic advantages:

- No clean room facilities required: modest implementation requirements,
- As the interaction solar radiation/nano-TiO₂ is isotropic, the solar conversion is independent from the angular daily solar radiation,
- The solar conversion efficiency increases with temperature,
- The cell can be deposited on flexible and plastic substrates,
- No shortage or cost limitations of the raw basic materials,
- Can be integrated both as window or roof type solar panels,
- Based on cost effective nano-scaled materials for which Africa is a major mining producer: Titania «TiO₂», Zinc oxide «ZnO» and Ruthenium «Ru»,
- Existing screen printing machines can be used,
- Flexible & light-weight,
- Can be used in many applications, different shapes & colors,

Sensitized Solar Cell

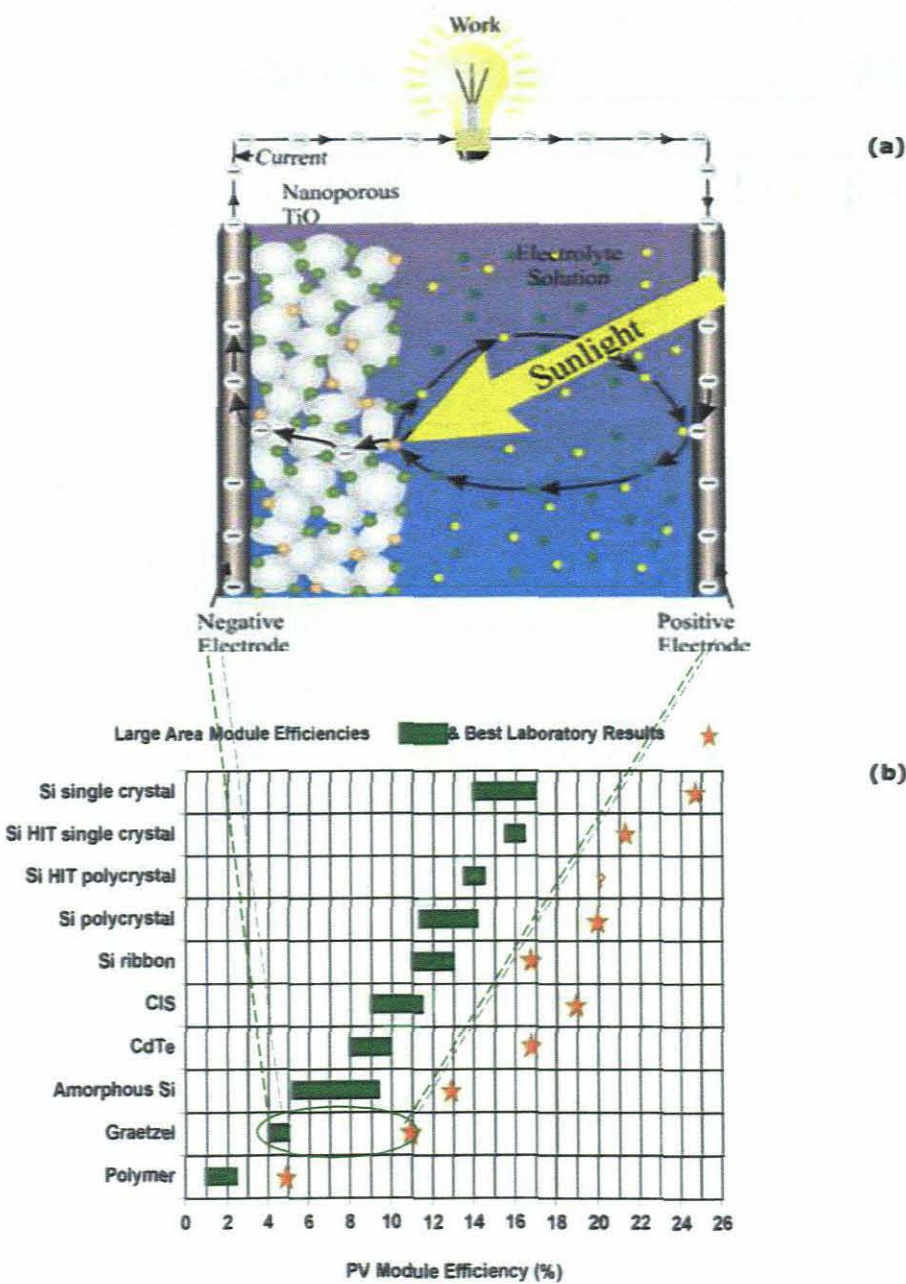


Figure 1: The solar conversion can take place from both DSC cell's faces.

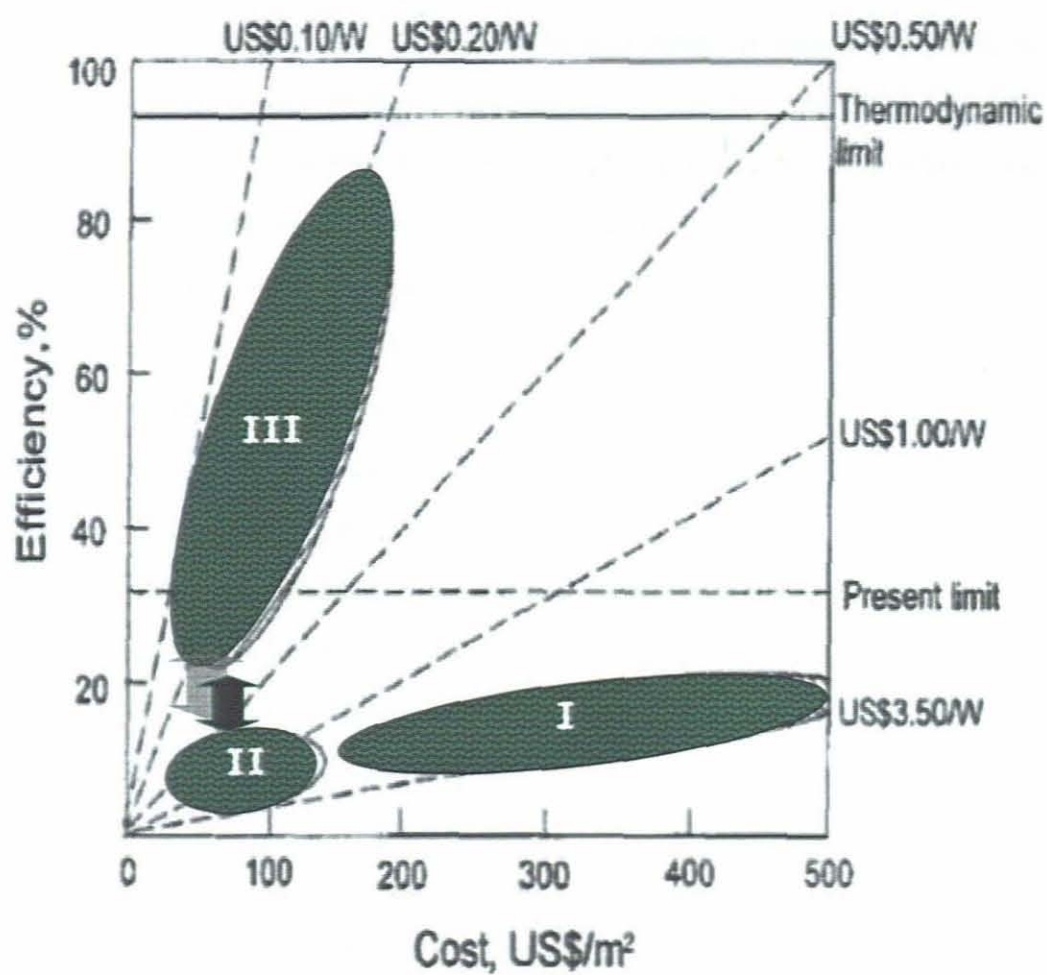


Figure 2: Variation of cost with efficiency in regions I, II, and III.

Taking into account that the average annual high solar irradiance flux exposure in the south which is about 1600-2500 kWk/m² in general and ~1600-2200 kWh/m² in South Africa specifically [Figure 3], this DSCs technology is indeed promising in particular within the current energy shortage supply within the rural areas. Overall, the market of solar cells has reached \$4billion in 2006 and as much as \$10 billion by 2010 according to the World Energy Council. Currently, it is asserted that Bulk crystalline Si devices would remain dominant for the near term. As the nano-TiO₂ DSC technology matures, it is projected that it would be a component in the market share of the crystalline Si devices. If the current maximum rate of conversion in laboratory prototypes is about 10-11%, the mass produced nano-TiO₂ DSC units in industry exhibit far small conversion rate, generally less than 6% on solid substrates and around ~4.8% on plastics. To be market competitive in the South-South in particular relatively to the well established Si & CIS technologies, this efficiency limitation of nano-TiO₂ DSCs have to be improved by an adequate and engineered design in specifically the nano-sized TiO₂ particles and their spatial organization. TiO₂, which forms the core component of DSCs, is regarded as the first common wide band gap semiconductor that has been studied and applied in efficient DSCs because other oxide materials such as SnO₂, ZnO, Nb₂O₅, and SrTiO₃ were found to be less efficient [Cha-2005]. In the early DSC prototype, Grätzel introduced a porous nanocrystalline «sponge like»TiO₂ electrode structure so to increase the internal surface area of the electrode to allow a large enough amount of incident solar radiations to interact with the nano-scaled TiO₂ electrode and electrolyte at the same time [Figure 1.a]. These common electrodes were produced by the deposition of a nano-sized TiO₂ layer on a transparent current collector yielding a porous geometry [Cha-2005]. As indicated in Figure 1.a, the electron-collection layer in this solar cell devise is typically a ~10 µm thick nanocrystalline TiO₂ film comprised of a three dimensional network of interconnected 15-20nm sized nanoparticles coated with a

dye monolayer. Films with such large surface area enables efficient light harvesting that in turn maximizes the amount of photo-generated charge carriers [Cha-2005, Pau-2006]. The structural disorder at the contact of two crystalline nano-particles results in an increase of the scattering of the photo-generated electrons, thus minimizing the electronic free mean path and the electronic mobility. As a consequence, and in addition to the well established low optical absorption cross section of the dye monolayer coating. There are two encountered major problems reported regarding this porous geometry: the high area cross-section for recombination of the photo-injected electron with the holes that are transferred to the electrochemical mediator and the image field opposing the separation process that is distributed inside the nanoporous electrode [Cha-2005].

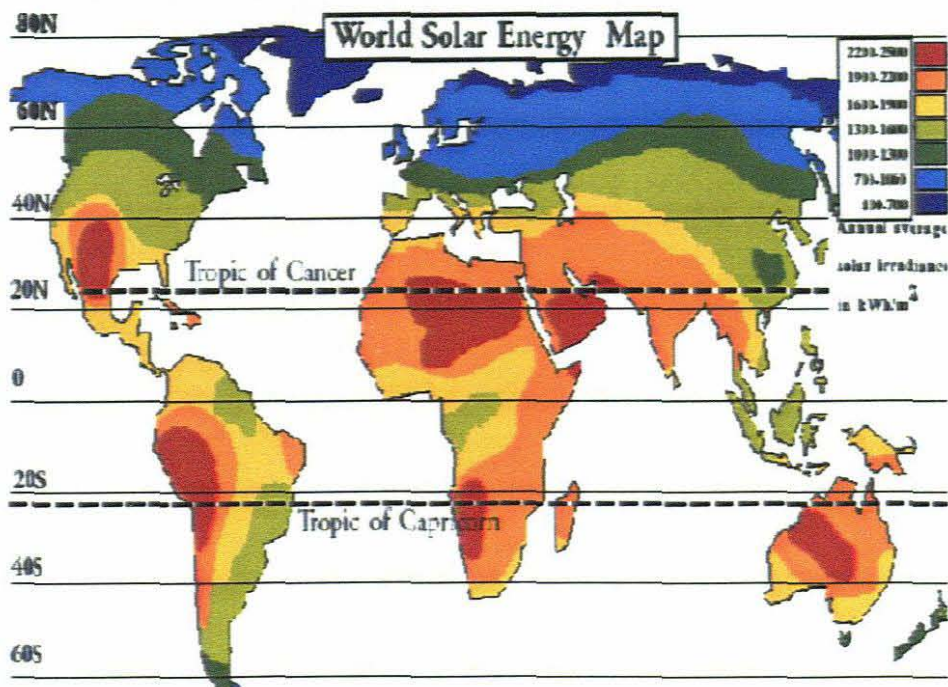


Figure 3: The world solar energy map illustrating annual average solar irradiances across the world.

Due to the disordered aspect of the nano TiO_2 network, it is also found that the electron transport is a limiting factor of the performance of these nanoporous electrodes, hindering progress in achieving higher efficiency [Cha-2005]. Thus several studies are instead focusing on replacing this TiO_2 nano-particles disordered network by a coating with either well ordered network or with shape anisotropy 1-D TiO_2 network made of ordered or oriented one-dimensional nanostructures such as nanotubes or oriented meso-porous arrays, aligned perpendicular to the collection transparent conducting oxide substrate. As shown recently, this geometry could potentially improve the charge-collection efficiency by promoting faster transport and slower recombination [Cha-2005, Bro-2006, Zhu-2006] [Figure 4]. Hence, ordered meso-porous nano- TiO_2 and arrays of shape anisotropy TiO_2 nanorods, nanotubes or ordered mesoporous arrays would exhibit less interfacial scattering and therefore a larger life time in addition to possible light trapping [Figure 5]. Both tubular and ordered porous structures of nano- TiO_2 would enhance the absorption efficiency of the dye large molecules by enhancing artificially their optical absorption cross section as well as allowing a better electronic transport (enhancement of the carriers free mean path).

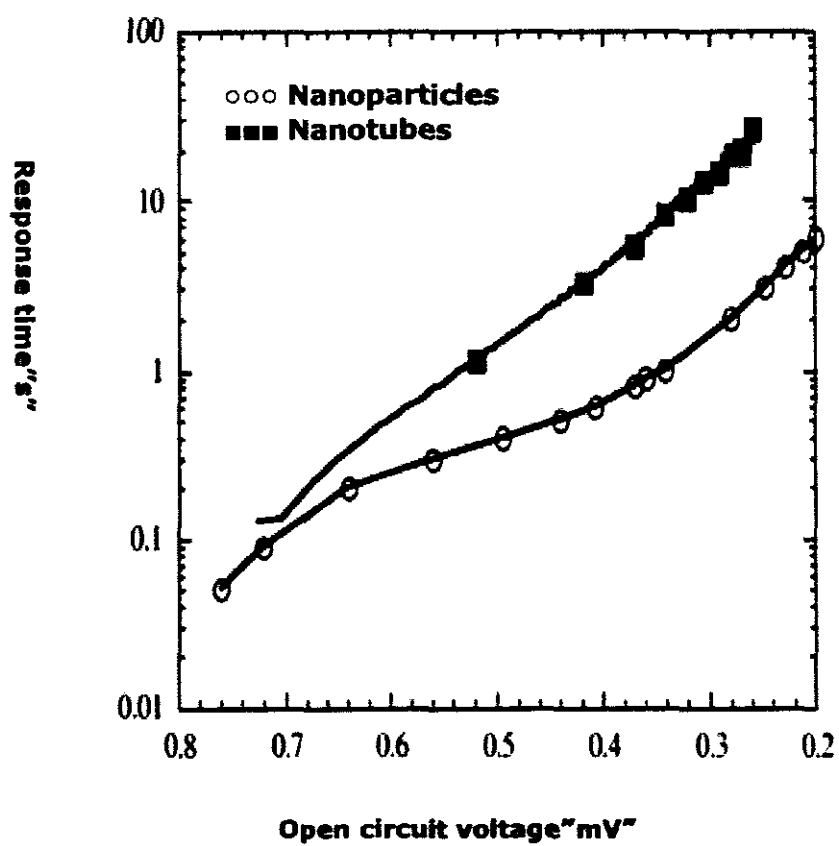


Figure 4: Response time vs. open circuit voltage for nano-particles and nano-tubes [Bro-2006].

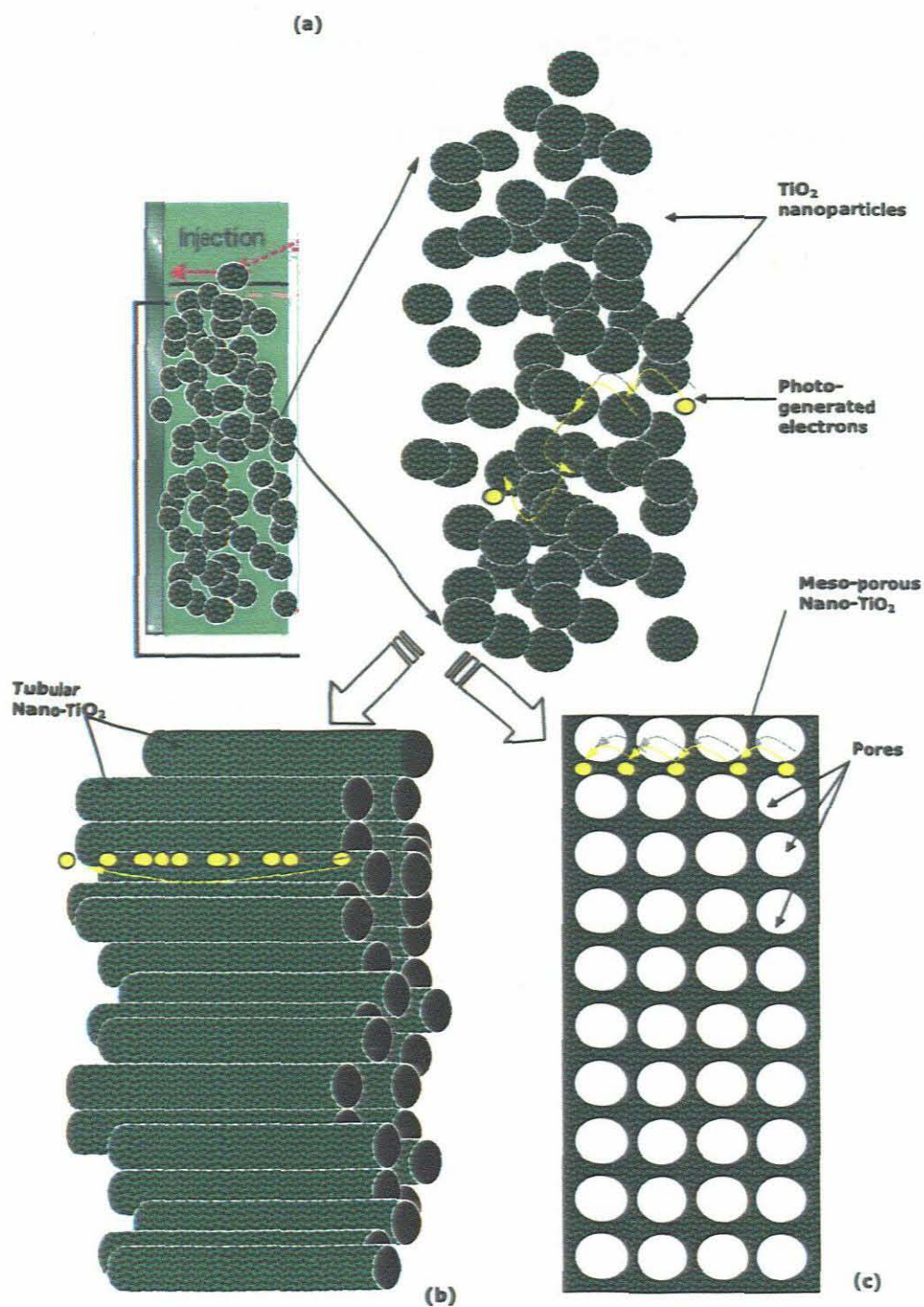


Figure 5: Schematic diagram showing the electron transport across (a) random oriented spherical TiO_2 nanoparticles, (b) ordered TiO_2 nanoporous arrays and (c) meso-porous nano- TiO_2 .

1.1 Objective and scope of the dissertation

This project aims mainly to investigate the morphological, crystallographic and room temperature optical properties of meso-porous TiO_2 arrays for the enhancement of the rate of photo-conversion in TiO_2 based dye sensitized solar cells. As for tubular systems, due to the ordered configuration of the meso-porous nano- TiO_2 , the electron transport following the electron-hole creation is expected to be more effective with a longer lifetime. In addition, if oriented, such a meso-porosity configuration would enhance the optical absorption cross section of the dye coating in addition to a possible light trapping mechanism. As indicated in Figure 4, in terms of current density, ordered/1-D nano- TiO_2 systems exhibit a two fold increase in short-circuit current density compare to standard nano-particles in standard dye-sensitized solar cells [D-Ye-2004, Pou-2005, Bro-2006]. According to the recent investigations done by several authors, highly ordered porous or tubular TiO_2 nano-systems could offer excellent pathways for electron transport with superior lifetime values, in effect acting as «electron highways» for directing the photo-generated electrons to the transparent conducting oxide layer «TCO». In addition, designing ordered nano-porous arrays of nano- TiO_2 would facilitate the transport of electrons to the back contact through the pathway rather than a random transport across spherical nano-particles [Figure 5]. It is also believed that such ordered porous/tubular nano- TiO_2 would permit vectorial charge transfer from the solution to the conductive substrate, thereby minimizing the losses incurred by charge-hopping across nano-particle grain boundaries [Pau-2006]. Figure 6 sustains such an assertion. While the electron injection and the dye regeneration are splitted in time while being in the pico and nanosec regimes respectively ($4 \cdot 10^{-12}$ and 10^{-10} s respectively), the electron transport and interfacial recombination are both within the time range of 10^{-4} - 10^{-2} s [Figure 6]. Hence there is a net competition between the

electron transport and the loss mechanism due to the interfacial recombination. This double phenomenon can be described via the electron diffusion length L given approximately by

$$L = \sqrt{D \tau}$$

where D and τ are the electron diffusion coefficient and the electron lifetime respectively. Thus, a tubular or ordered meso-porous nano TiO_2 structures could minimize the electronic scattering and hence the lifetime and consequently a higher rate of conversion. As an indicative value, it is expected that typical values for high performance dye solar cell TiO_2 nano-crystalline based cells i.e. with rate of conversion of $\sim 10\%$, L should be about $100\mu\text{m}$ for D and τ of $10^{-4} \text{ cm}^2/\text{s}$ and 1s respectively.

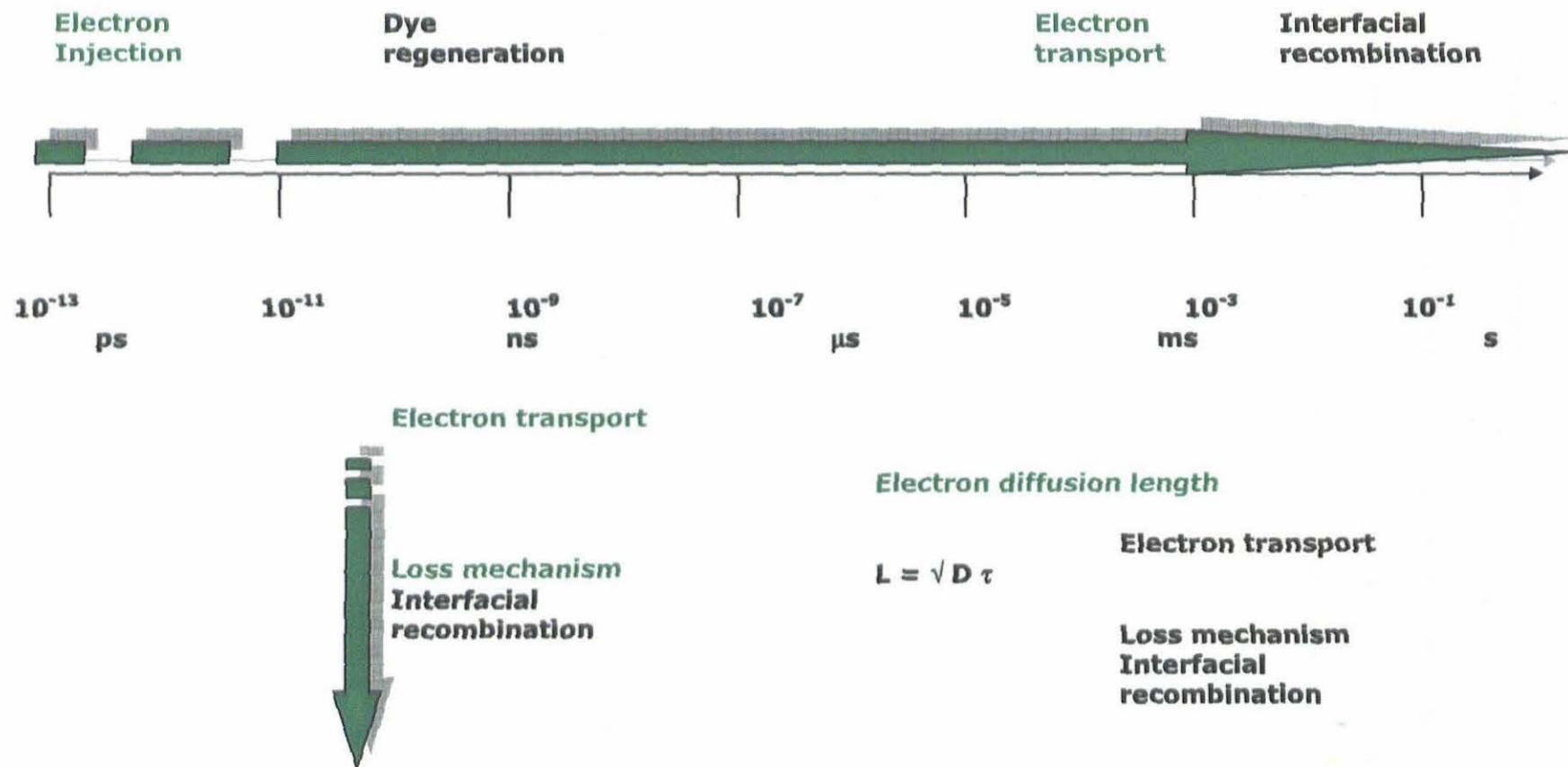


Figure 6: Dynamic competition between the transport of the photo-generated electrons and their interfacial recombination.

1.2 Dissertation layout

Chapter 2 covers the background on Dye Solar Cells technology and the related physical phenomenon. DSCs components including sensitizing dyes, electrolyte, and electrodes (porous nanostructured semi-conducting electrode and counter electrode) are also discussed in this chapter. Since DSCs technology imitates natural photosynthesis mechanisms, the detailed information on process of photosynthesis is also presented.

Chapter 3 highlights the physical and crystallographic properties of TiO_2 .

Chapter 4 gives a literature review on the synthetic approaches of choice that were considered in this project to synthesize highly ordered meso-porous nano- TiO_2 so to enhance the free mean path of photo-generated electrons. The combination of sol-gel and evaporation induced-self assembling (EISA) methods including triblock copolymer as a template is specifically presented in this chapter. Information on synthesis of ordered mesoporous nano- TiO_2 is also covered. Detailed information on mesoporous TiO_2 films focusing mainly on formation of mesoporous TiO_2 films using a block copolymer as a template is also provided in this chapter.

Chapter 5 describes the method used for preparation of the investigated mesoporous nano-arrays of TiO_2 anatase films and reports the various experimental studies and measurements as well as the corresponding discussion.

CHAPTER 2

2. DYE-SENSITIZED SOLAR CELLS

2.1 Natural photosynthesis

As well established, Gratzel dye sensitized solar cells are based on the natural photosynthesis phenomenon yet natural photosynthesis occurs with stunning efficiency in comparison to the presently state of the art silicon based solar cells. To enhance the rate of conversion of the dye solar cells based nano-TiO₂, it is worth to mimic as closely as possible the natural photosynthesis. The natural photosynthesis system is based on effective redox reactions. The natural photosynthesis uses solar energy to generate and transfer electrons from water to energy rich compounds. These transferred photo-generated electrons via flora leaves are then used in secondary processes to sustain life and to form all the valuable products formed by photosynthetic organisms. As shown in Figure 7, the photosynthesis mechanisms in plants starts in the nano-scaled thylakoid membranes of chloroplasts containing a significant number of integrated photosystems within the flora leaf. Such a typical natural photo-conversion system consists of an antenna and a reaction center containing chlorophyll molecules. The antenna is made up of light harvesting dyes which absorb photons and then funnel the energy to chlorophyll A molecules found in the reaction center [Liz-2004]. Chlorophyll A is the principal light absorbing pigment of photosynthetic whereas Chlorophyll B and carotenoids [Figure 8.a] are secondary antenna pigments which extend the absorbing spectral range of the photosystem. As indicated in figure 8, the high optical absorption of the different chlorophyll compounds in addition to the efficiency of the charge transfer makes the natural photosynthesis occurring with a stunning efficiency relatively to state of the art man-made optical systems [Figure 8.b]. Photon energy, absorbed by the pigments in the light harvesting antenna, is transferred to the reaction center chlorophyll A. This

occurs without electron or photon transfer but through resonance energy transfer. Upon energy absorption, the reaction center chlorophyll A molecule is raised to an excited energy state. The excited chlorophyll A then donates an electron to a primary electron acceptor, which then transfers the electron to another molecule, starting the glucose synthesis reaction. The oxidized chlorophyll A is regenerated by a reducing molecule and the process starts over.

Imitating and using the fundamental light harvesting mechanisms of the natural photosynthesis, as mentioned previously, the DSC technology converts light energy to electrical energy via redox reactions involving photosensitive artificial dyes coated nano-particles of TiO_2 . Such a nano-scale structure of the TiO_2 particles enhances consequentially the effective surface of these nanoparticles to be coated by a dye by many orders of magnitude & thereupon empowers significantly the rate of light conversion.

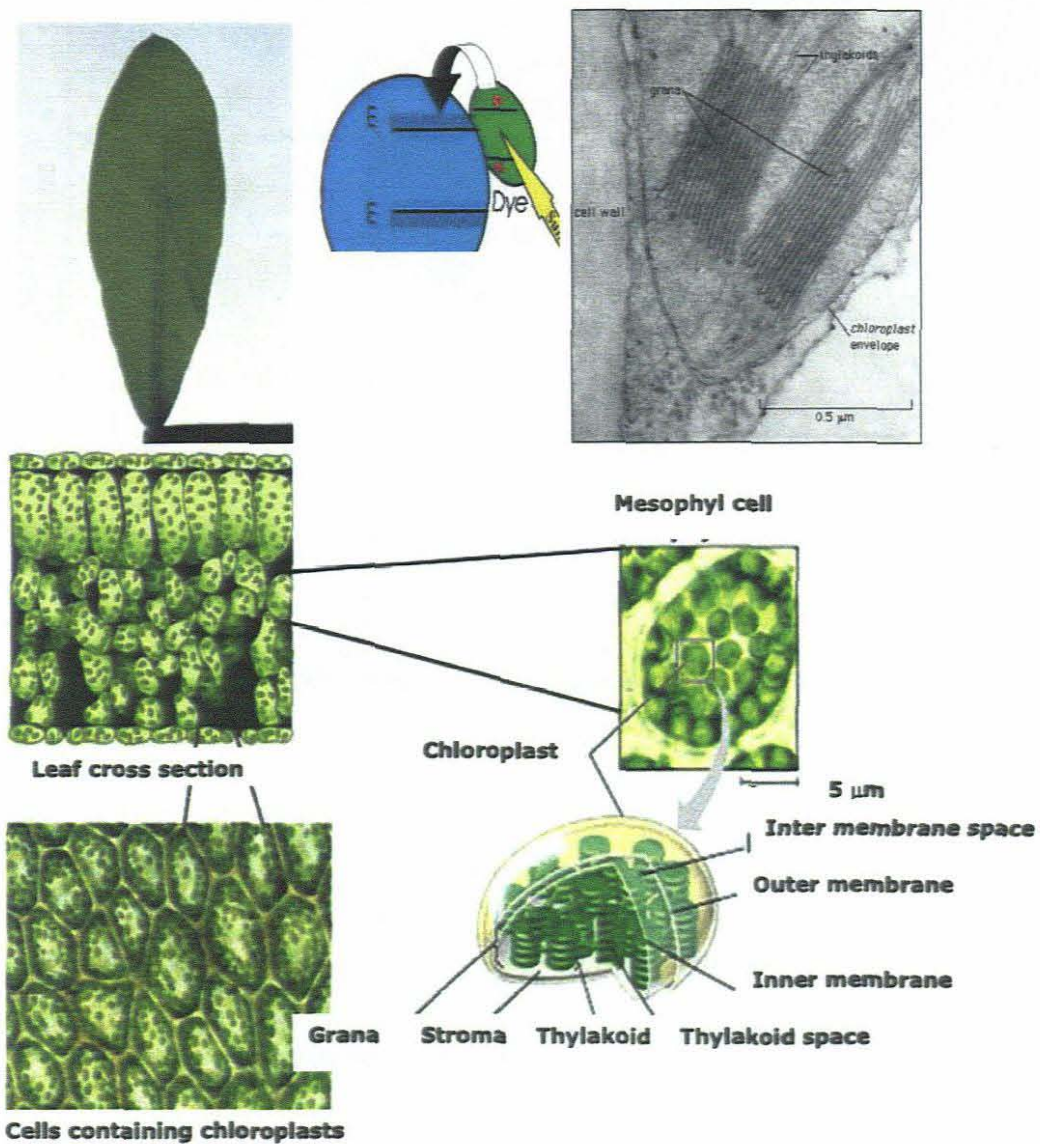
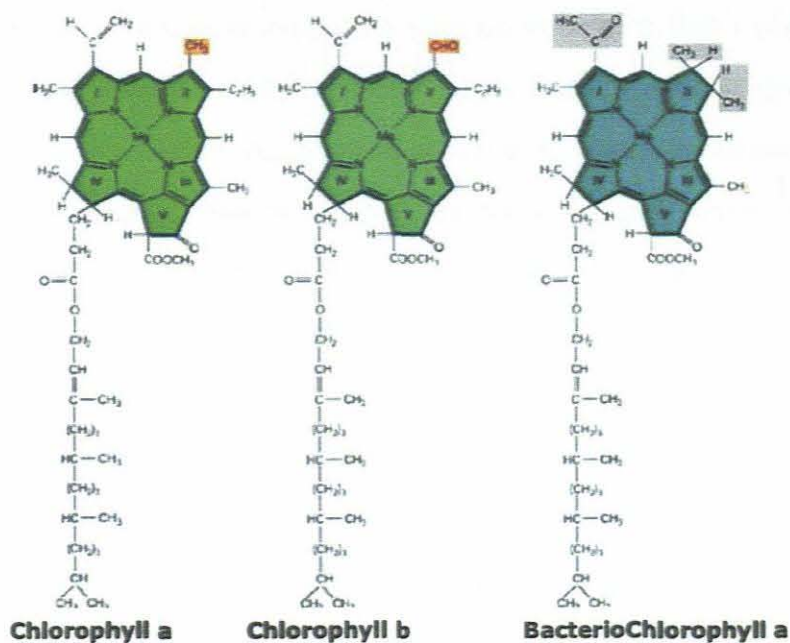


Figure 7: Photosynthesis mechanisms in plants

(a)



(b)

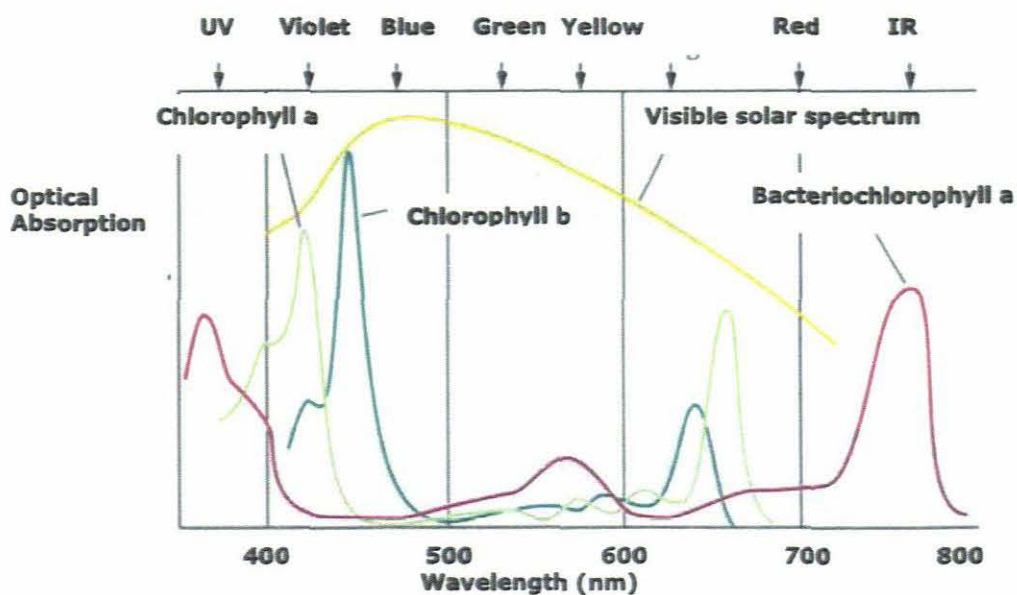


Figure 8: Molecular configuration of the natural chlorophylls and their respective optical Absorption spectra [Liz-2004].

2.1.1 Artificial photosynthesis and principle of the DSCs technology.

The concept of dye-sensitization was initiated in order to find a photochemical solar cell which is based on a semiconductor that is stable against photocorrosion and yet absorb in the visible region [Hal-2002] and emits photo-generated charges. However, several number of metal oxides seem to qualify for this matter, but most of them exhibit a cut-off wavelength in the UV range. However, organic dyes are used to act as sensitizers as they absorb a broader range of the solar spectrum [Qia-2001, Bro-2006]. It was then thought that the significant way of extending the spectral absorbance of the oxides is to adsorb dye molecules with a significant extinction coefficient in the visible spectrum on the semiconductor oxide surface. For efficient solar energy conversion, the concerned artificial dye is required to have high absorption coefficients over the whole spectral region; from UV to NIR and even the far IR region [Qin-2001]. However, very limited number of dyes is able to give high photocurrent quanta yields being still reasonably stable against photo-degradation [Qin-2001].

DSC's simple illustration can be illustrated as shown in Figure 9. It is based on the mechanism of a regenerative photo-electrochemical process. It consists of two transparent electrically conducting glass electrodes generally Fluorine or Indium doped Tin oxide so called FTO or ITO respectively «average film thickness is about 0.5 μm ». One of the two working electrodes is coated with a high porous nanocrystalline TiO_2 «~20 nm in average diameter» film. A monomolecular layer of sensitizing dye on the nanocrystalline TiO_2 surface absorbs the incoming light. The device is completed by a counter electrode of platinum deposited onto the second conducting electrode. An organic solvent based electrolyte containing the redox-couple iodide/tri-iodide is inserted between the electrodes. Electron injection kinetics

and reduction of the oxidized dye are fast compared to degradation reactions. When operating in the solar cell, the dye is excited by the visible light after which electron injection occurs into the TiO_2 semiconductor nanocrystals. The oxidized dye molecules are then regenerated by the iodide ions in the electrolyte which are in intimate contact with the dye. As it is sustained by Figure 10, the IPCE or rate of conversion of the nano-crystalline based TiO_2 solar cell is very high over a large spectral range relatively to the same solar cell with a bulk TiO_2 . The average value of the IPCE is about 80% for the nano-crystalline structure while it is less than 0.15% for the corresponding bulk structure. The nano-structured form allows a larger dye coating and hence a significant photo-generated electrons. The excited and oxidized states of the sensitizer are the reactive compounds. The rate constants for charge injection and iodide reduction are at least $10^7/10^8$ times faster than the degradation pathways which therefore should guarantee a turnover of about 10^7 without a significant degradation of the dye.

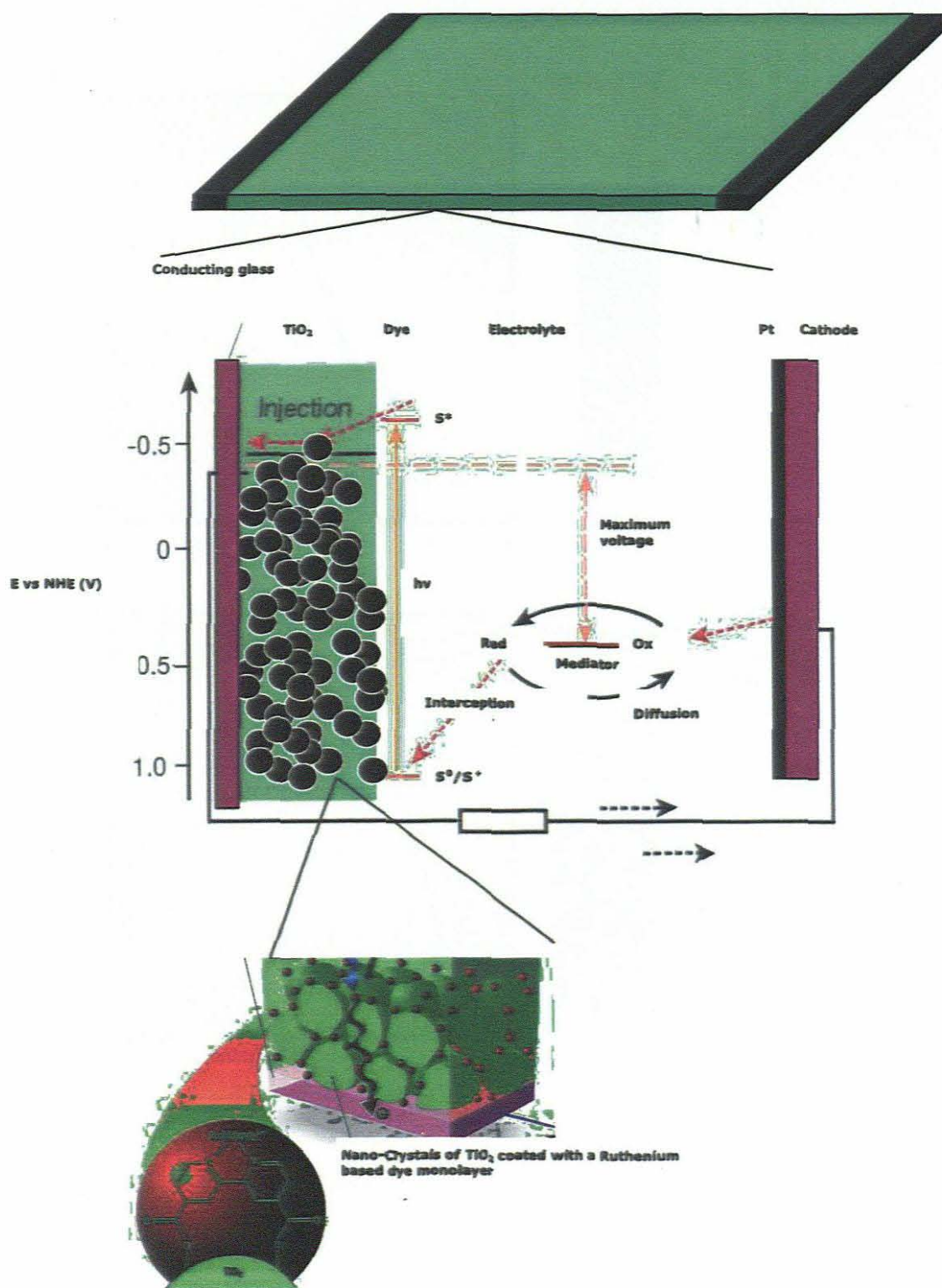


Figure 9: Schematic representation of DSCs.

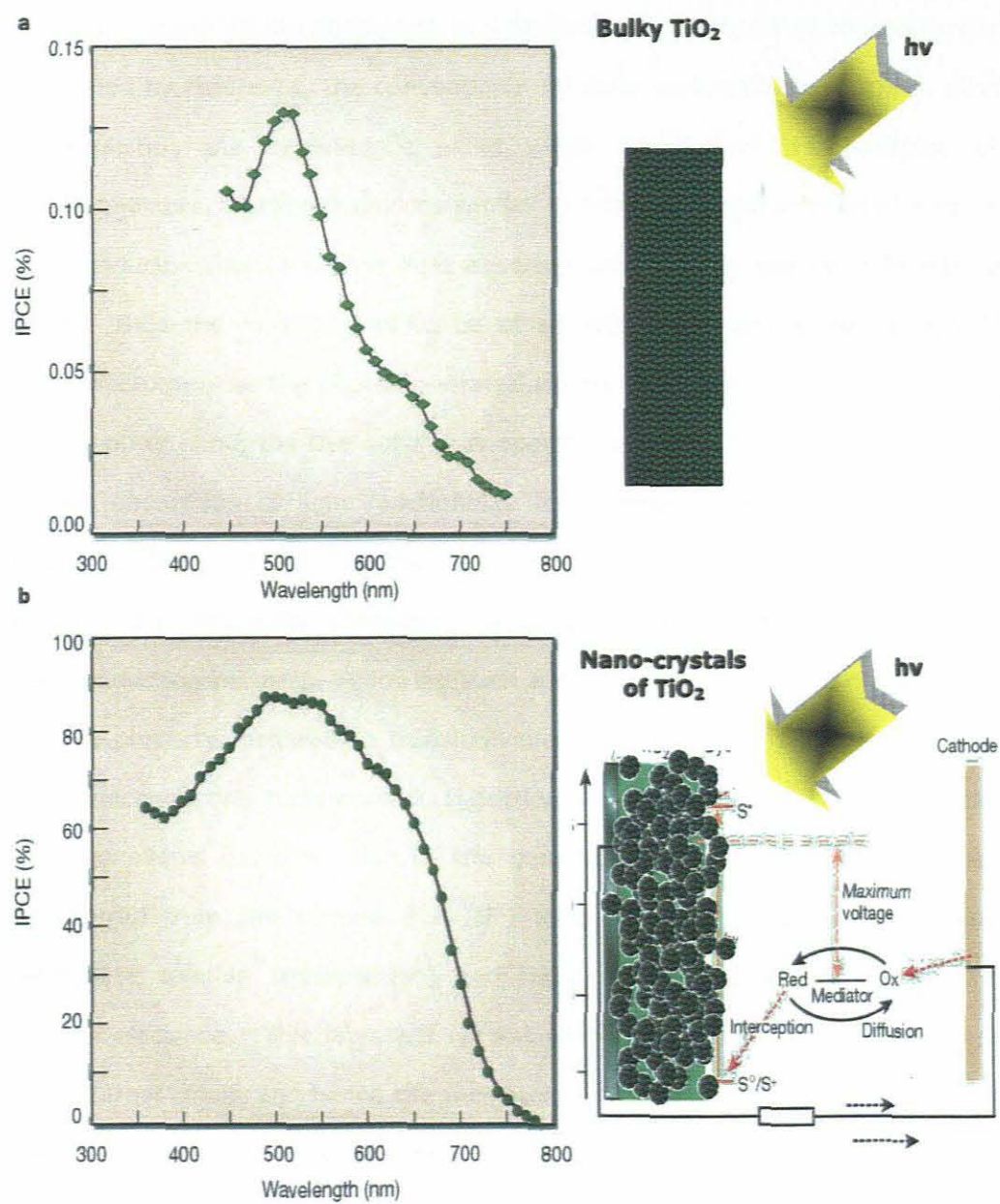


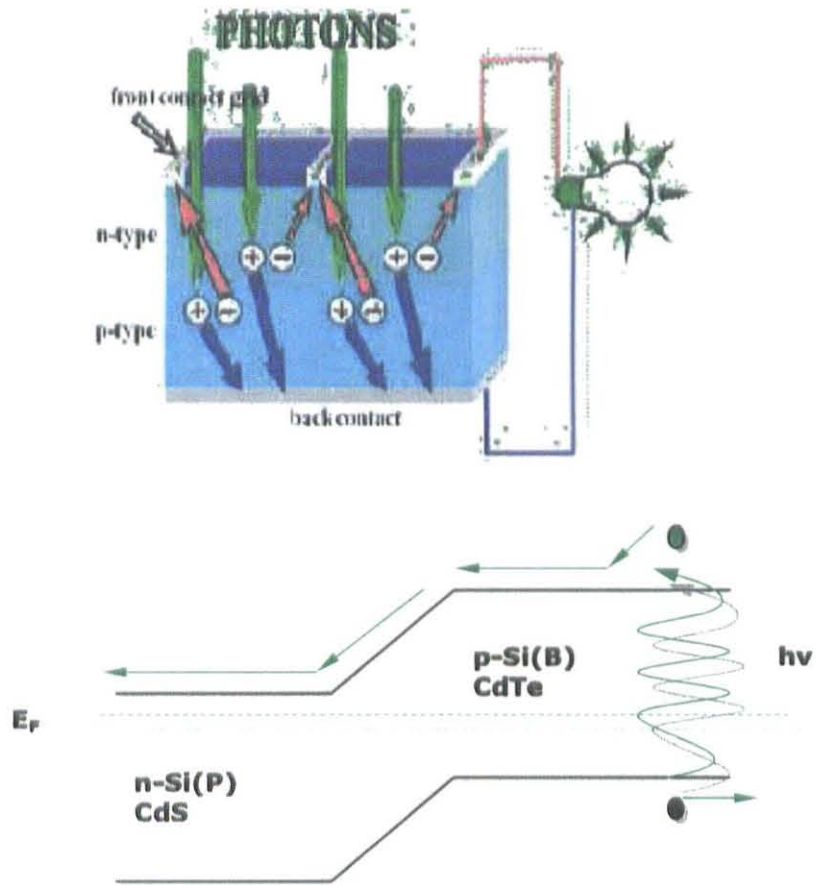
Figure 10: IPCE curves illustrating the rate of conversion in (a) bulk TiO_2 and (b) nano-crystalline TiO_2 based solar cells.

This is one of the major differences with standard PV solar cells. The Gratzel dye solar cell separates the absorption of light from the transport of charge carriers. As illustrated by Figure 11, the conventional PV solar cells convert light into electricity by exploiting the photovoltaic effect which appears at the interface of two semiconductors. These are devices similar to transistors and integrated circuits. The semiconductor acts both as a light absorber and charges separator (electrons and holes). Thus the material has to be of a very high chemical purity and defects exempted otherwise the photo-generated electron-hole pairs before their separation. On the other hand, the Dye solar cells operate differently from the standard PV cells as the absorption of light functionality is disconnected from the electric charge separation [Figure 11.b]. The absorption of solar light is instigated by a monolayer of a dye (S) adsorbed chemically onto the surface of the nano-crystalline semiconducting particles. Following such a photonic absorption, the dye with a well defined property, generally a transition metal complex, can transfer an electron to the semiconducting nano-crystals (injection process). The electric field within the material allows the extraction of the generated electron. The positive charge is transferred from the excited dye (S^+) to a redox mediator present within the electrolyte solution (interception) and thus it is guided to the Platinum coated counter-electrode. This later will recombine with the electron generated traveling the external circuit and hence the mediator is reduced and the circuit is closed. The maximum theoretical voltage which can be delivered by the set up corresponds to the the difference between the redox of the mediator and the Fermi level of the semiconductor as indicated in Figures 9 and 11.b. The recombination between the injected electron in the conduction band of the semiconducting nano-crystals and the hole in the oxidized dye is very slow compared to the reduction of this later by the mediating solution. In addition, the electron-hole recombination in the semiconductor, which affects tremendously the efficiency of the standard PV cells

does not exist as there is no hole in the valence band corresponding to the photogenerated electron in the conduction band. Consequently, the rate of conversion stays unchanged somehow even under very low illumination such as a cloudy sky which is not the case of standard PV systems. In terms of electron injection-recombination, as indicated in Figure 6, the various time scales within the dye solar cell structure can be summarized as:

- (i) Electron injection rates: 50%: $<150\text{fs}$, 50%: time constant of $1.2\pm0.2\text{ps}$
- (ii) Charge recombination rates: ns to ms, dependent upon applied bias voltage (EF)
- (iii) dye re-reduction rate : 100ns

(a)



(b)

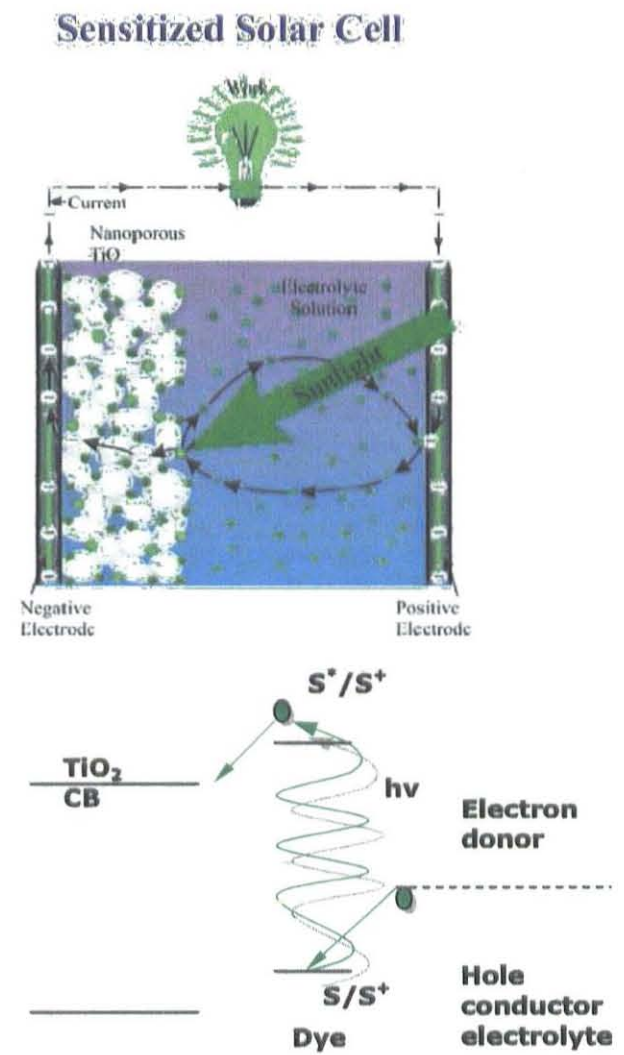


Figure 11: Charge creation and charge separation in (a) standard PV Si based and (b) a typical dye solar cell

2.2 Porous nano-structured semi-conducting electrode

Titanium dioxide «TiO₂» represents the pre-disposed semiconductor for the Gratzel dye solar cells in its nano-structured films form. Due to its very large band gap «3.2 eV», it is unsensitive to the visible solar radiations with an energy cut off located within the UV spectral range. It can be sensitized by a diverse family of dyes among which some allow an IPCE close to unity. TiO₂ is a standard material with vast technological applications as it will be stressed in chapter 3. It is used traditionally as a photocatalytic support and as a pigment in paint and paper industry as well as a UV protective cream [Mor-2006]. Its non toxicity allows its employment in cosmetics and tooth paste. Recently, and in connection with the combination of its surface tension and photocatalytic properties, it is used as a self-cleaning nano-coating of commercial glass smart windows.

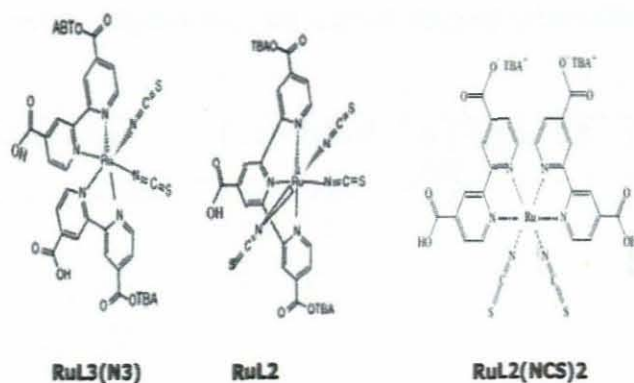
In the Gratzel dye solar cells technology as an electrode, TiO₂ is used in its nano-particles scaled discontinuous form in a percolating network structure. The production of nano-scaled TiO₂ is described within chapter 4. The production of the porous nano-crystalline sponge-like TiO₂ on transparent conducting oxide «TCO» electrodes deposited onto glass substrates is generally processed by a standard procedure of serigraphy. During this serigraphy phase, a suspension of nano-crystalline TiO₂ is deposited onto the coated TCO glass leaving the solvent evaporating. This step is followed by an annealing at about 450°C which ensures the formation of interconnected dense nano-porous film of TiO₂. The nanometric size of the particles «~10-30 nm» bestows to the nano-porous interconnected film a roughness factor of about 400 by μm thickness. Hence a nano-structured TiO₂ layer of about 10 μm exhibits an internal surface equivalent to 10³ times than a continuous TiO₂ film. Such a colossal surface /volume area favors a large surface to be coated

with a dye monolayer and hence a high optical absorption and therefore a high photogenerated electrons.

2.3 Absorbing dye complex

With the ultra porous nano-TiO₂ electrode, the dye constitutes the second key element of the Gratzel dye solar cell. It must exhibit an extended optical absorption spectrum as wide as possible covering the VIS and the NIR solar range. In addition, it must be able, at the excited state to inject the photogenerated electron to band-gap of the TiO₂ semiconducting nano-particles. Finally, it must exhibit an excellent stability which would allow millions of excitation-oxydation-reduction cycles necessary for a long term cell operation lifespan. The organic based dyes tested so far reported in the literature are generally affected after thousands of cycles and thus are not potential candidates. The transition metals complexes in general and those based on Ruthenium and Osmium specifically are excellent candidates. The first efficient dye that was used with the nanocrystalline solar cells was cis-RuL₂-«NCS» 2, where L stands for 2,2'-bipyridyl-4,4'-dicarboxylic acid, also called N3 dye [Figure 12]. This dye has been the top choice for dye-sensitized solar cells and has shown the best performance. Recently, the tri "cynato"-2, 2', 2''-terpyridyl-4,4', 4''-tricarboxylate" Ruthenium "II" also known as black dye exhibits better near-IR performance. Tolvanne and Agrell [Gre-2004] have used a two-fold deprotonated form of N3 called N719 [Figure 12.a]. This dye has a tendency of producing higher photovoltages than N3 and besides it is regarded as one of the most efficient and most currently studied dyes for nanostructured solar cells [Table 1]. Figure 12.b reports the IPCE responses versus the wavelength in the spectral range 300-800 nm of nano TiO₂ cells colored by the different mentioned above Ruthenium complexes.

(a)



(b)

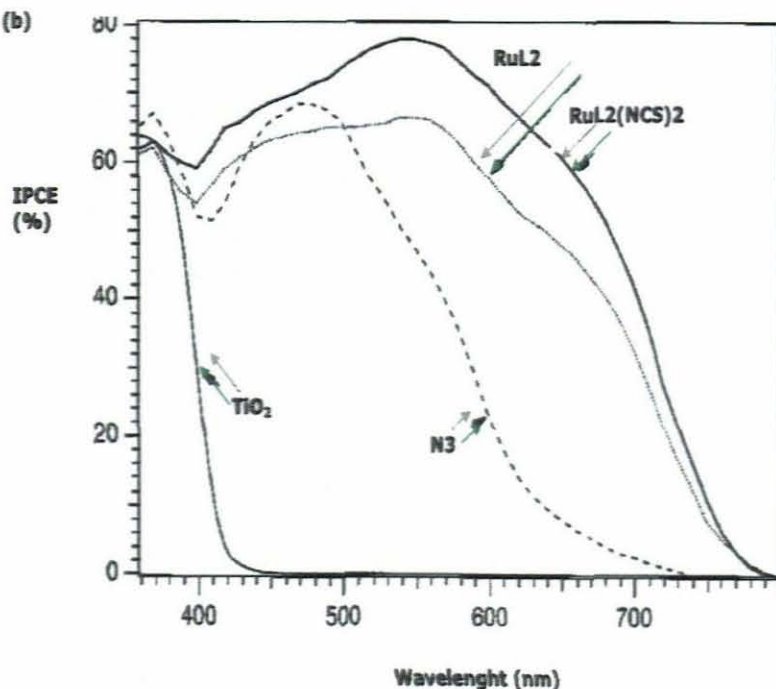


Figure 12: (a) The molecular structure of the dyes N3, Black dye and N719 used in the EPFL Gratzel initial cells. (b) Spectral response «incident photon to current conversion efficiency» curve of dye-sensitized solar cell for difference dyes compared with the spectral response of pure TiO₂ electrode [Hal-2002, Tol-2003, Gre-2004].

Table 1: Most currently studied dyes for nanostructured solar cells.

Institution	nano-oxide	sensitizer	η (%) at 1.5 AM	Reference
NREL	nc-anatase TiO ₂	Iron (Fe)-based Ru dye	9.2	[Deb-1998]
OSU	anatase TiO ₂ nano-particles	N-719	6.7	[Tan-2006]
OSU	anatase TiO ₂ nanowires	N-719	8.6	[Tan-2006]
AIST	nc-Nitrogen doped TiO ₂	N-719	8	[T Ma-2005]
IAE	mesoporous TiO ₂ nanorods	N-719	7.12	[Pav-2007]
	mesoporous nc-TiO ₂	Z-955	8	[Wan-2004]
IAE	nc-mesoporous TiO ₂	N-719	8.06	[Nga-2006]
EPFL	mesoporous TiO ₂ nanoparticles	K-77	9.5	[Kua-2007]
MRL	highly ordered TiO ₂ nanotube arrays	N-719	2.9	[Mor-2006]
LNES	anatase TiO ₂ nanotubes	Ru-535	5.64	[Flo-2007]
IAE	single-crystal like TiO ₂ nanowires	N-719	9.3	[Ada-2004]
IAE	anatase TiO ₂ nanowires	N-719	6.53	[Aso-2007]
EPFL	mesoscopic anatase TiO ₂	N-719	11.2	[Gra-2005]
ECN	nc-TiO ₂	N-719	2.3	[Som-1998]
NIMC	nc-TiO ₂	N-719	5.6	[Har-2001]
EPFL	nc-TiO ₂	N-719	11.1	[Wan-2006]
ECN	nc-TiO ₂	N-3	8.2	[Hin-2001]
IPP	nc-TiO ₂	N-719	5.69	[L Hu-2007]
CEA	nanoporous anatase TiO ₂	N-719	1.3	[Bel-2006]
IPP	nanoporous TiO ₂	N719	5.96	[Yue-2004]

One should note that at the maximum of the dye absorption, approximately each absorbed photon is converted to an electron. In connection with the optical absorption characteristics, it is found that dye exists in two redox states in the solar cell " R^{2+} and R^{3+} " [Hal-2002]. The valence level of neutral ruthenium " $Ru4d$ " contains eight electrons " d^8 " and therefore Ru^{2+} and Ru^{3+} have six and five d-electrons, respectively [Gre-2004]. Therefore, the highest occupied molecular orbitals are almost entirely of Ru and NCS character and the lowest unoccupied molecular orbitals are mainly of dicarboxybipyridine "dcbpy" ligand character [Gon-1996, Cac-2002, Goe-2003, Jia-2004, Gre-2004]. The Ru based dyes absorb light between 300-800nm and can be extended to the near infrared at about 900 nm as indicated in Figure 6 [Hal-2002, Gre-2004]. Moreover, two absorption maxima in the visible wavelength region, 400nm and 550nm "when absorbed onto the TiO_2 film" are due to metal to ligand charge transfer "MLCT" transitions, whereby an electron localized mainly on the Ru-NCS centre in the initial state, is transferred to the orbital set on the dcbpy ligands [Figure 12]. In addition to the required large and high optical absorption properties, the dye molecular complex should display a superior anchoring on the surface of the nano-crystalline TiO_2 [Mur-1995]. Indeed the bonding between dye and the TiO_2 should provide high stability, dense packing and efficient charge injections [Gre-2004]. As schematized in Figure 13, the distances of anchoring terminals of the Ru dye complexes are quasi identical allowing a good anchoring; they are about 1.00 nm and 0.98 nm for the dye and 1.023 for the TiO_2 nano-crystals surface atoms. The IPCE curves for cells sensitized with different dyes compared to naked TiO_2 electrode is clearly illustrated on figure 12. These curves show the efficient spectral sensitization in DSCs. However, the current efficiency of the cell is basically related to the 'height' of the IPCE curve, which depends on the charge separation and charge collection efficiency [Hal-2002, Tol-2005]. Several dyes have been extensively studied, for instance phthalocyanines [J He-2002] have

shown an excellent long-term stability, but due to surface aggregation phenomena and very fast electron recombination, the device performance was rather modest; 0.54% overall efficiency and 24% monochromatic incident photon-to-current conversion at the absorption maximum of 690nm. Balaban *et al* [Sch-2004] have recently suggested the usage of chromophores for photo-sensitization of the wide gap nano-structured semiconductor a self-assembling molecule that is able to bind to the surface and form a light-harvesting nanostructure at the same time. Thus, the self-assembled artificial antenna should have a broad absorption range and high extinction coefficients desirably over the whole visible region and into the near infrared. In addition, its ability to pass on the excitation via rapid energy transfer processes should not be affected due to non-specific aggregation. Usually, due to concentration quenching, the fluorescence of aggregated dyes is strongly quenched and thus the excitation energy transfer is hindered. Recently Ran *et al* [Pan-2007] successfully synthesized a novel family of dye complexes with of a mostly solid-state high efficient electro-conductive material comprising 1-methyl-3-propylimidazolium iodide, benzimidazole (BI), iodine and lithium iodide. In this electrolyte, BI acts as not only additives but also gelators. With its significant electrochemical properties, an overall efficiency of 3.07% was achieved under AM 1.5 (100 mW/cm²).

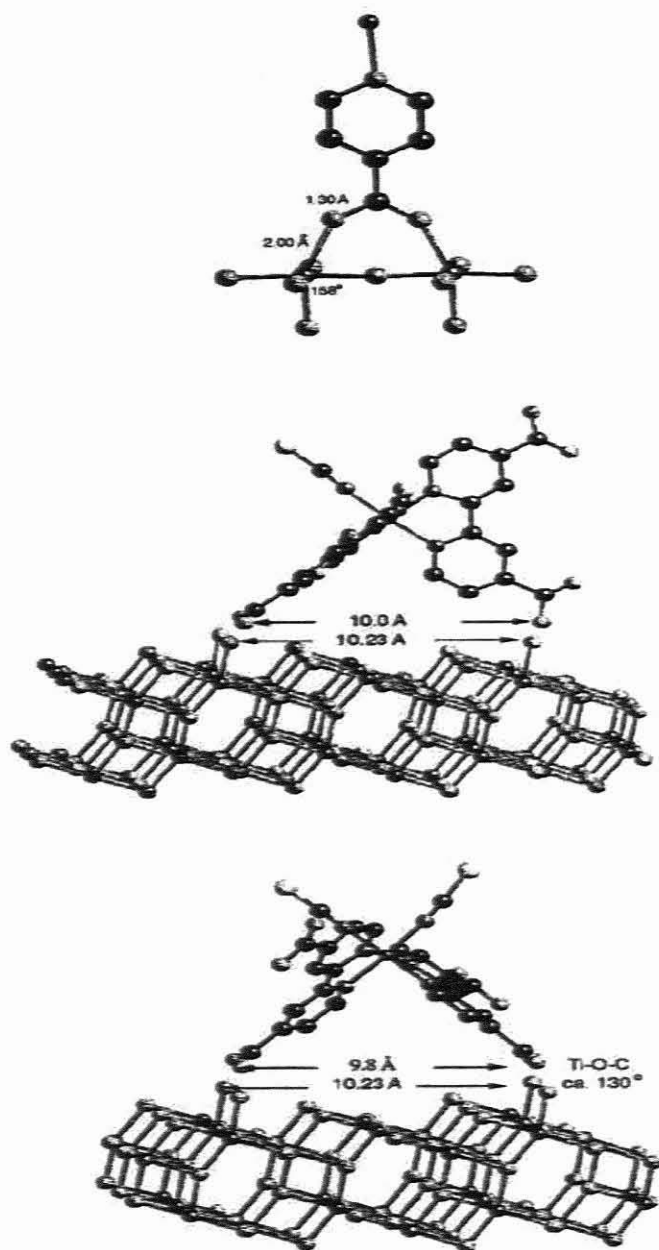


Figure 13: Importance of binding states between photosensitizing molecules and the TiO_2 surface for efficiency in a dye-sensitized [Mur-1995].

2.4 Electrolyte and counter electrode

In contrast to solid electronic conductors such as metals and semiconductors, the current liquid electrolyte is carried by ions [Gre-2004]. These ions are basically formed by the dissociation of salts in polar solvents. The electrolyte in the dye-sensitized solar cells consists of a redox couple, normally iodide/triiodide «iodine + Lithium iodine» dissolved in an organic solvent «Acetonitrile+ Tert Butylpyridine». The organic solvents are generally used instead of water based ones because the instability of the used dyes in hydrous media. The best actual solar cell that was first reported operate with the I_2/I^- or Br_2/Br^- couple due to slow kinetics for I_2 reduction on tin oxide based transparent electrodes « SnO_2 » and specially on TiO_2 surfaces [Gre-2004]. For high power DSC applications volatile electrolytes with low viscosity such as Acetonitrile are used and give the best performance [Figure 14]. Typically, the electrolyte consists of 0.5 M Lithium iodide, 50 mM Iodine and 0.3 M Tert-Butylpyridine in acetonitrile. The counter electrode which consists of a TCO coated glass in addition of a platinized surface layer ($5-10 \mu g/cm^2$) is submerged into the electrolyte solution covering the nano-porous TiO_2 working electrode.

During solar radiations exposure, the dye molecule emits a photogenerated electron which is injected in the TiO_2 nano-particles which in its turn channeled to the external circuit via the transparent conducting oxide of the working electrode [Figure 14]. This electron is re-injected in the electrolyte at the interface of the platinum-electrolyte of the counter-electrode. The dye recovers its initial state by receiving an electron from an iodide ion, in turn oxidizing the iodide to iodine. At the counter-electrode, the electron is transferred to triiodide in the electrolyte to yield iodine, and the cycle is closed by reduction of the oxidized dye by the iodine in the electrolyte.

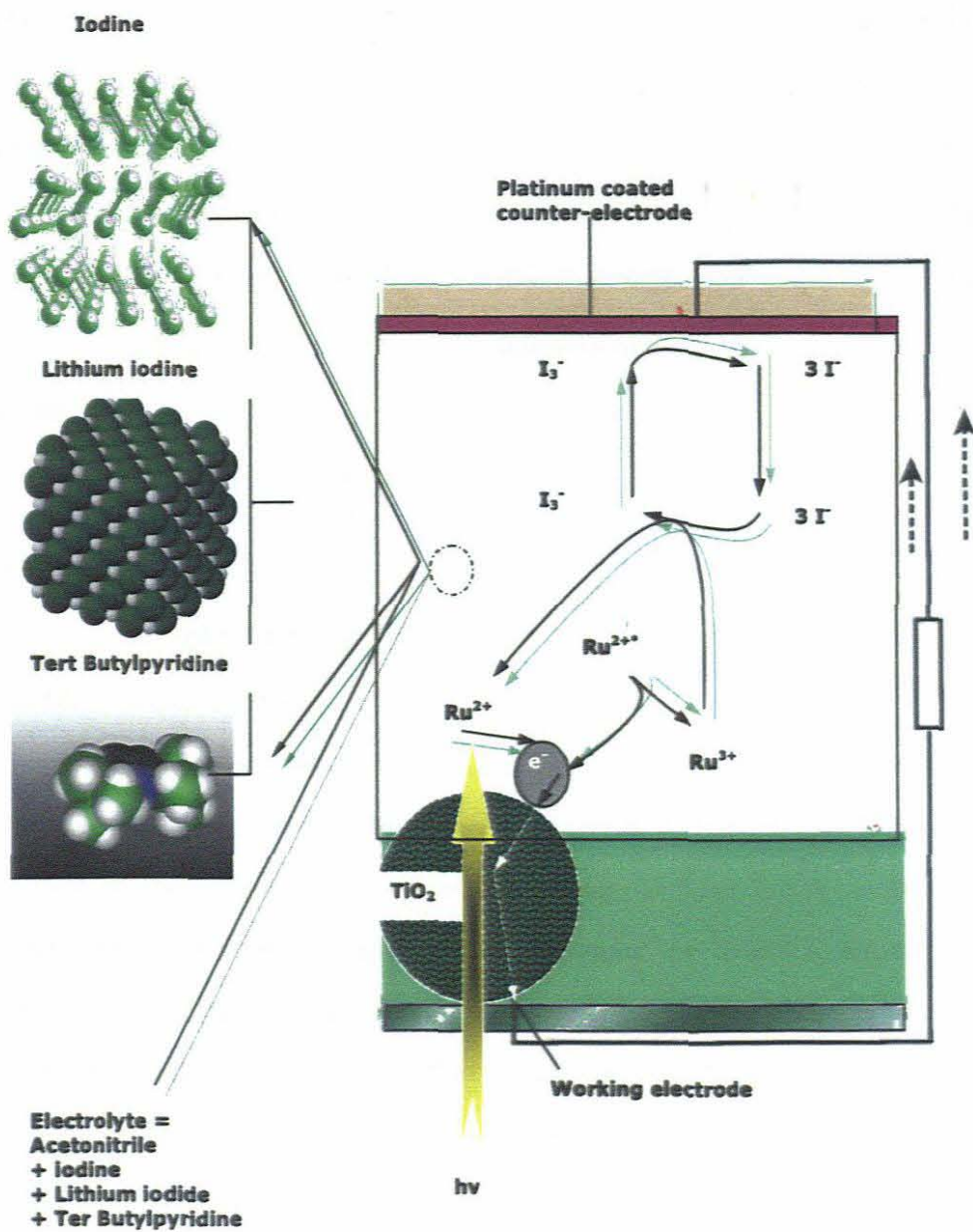
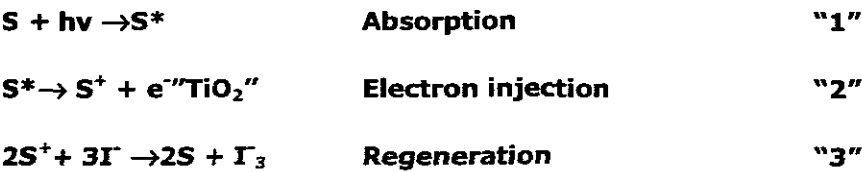


Figure 14: Operation of counter electrode in DSCs.

The operating cycle summarized in chemical reaction form below as follows [Hal-2002]:

Anode:



Cathode:



Anode:



The potential difference between the conduction band edge of the TiO₂ and the redox potential of the "I⁻/I₃⁻" pair in the electrolyte play an important role in determining the maximum theoretical value for the photovoltage at open circuit condition. Since the operation of the cell is regenerative in nature, no chemical substances are neither consumed nor produced during the working cycle, as visualized in the cell reaction [Hal-2002]. The photoexcitation occurs very rapidly within the femtosecond regime. It takes only 10⁻¹⁵s. After that, the electron is then injected into the conduction band resulting in a positively charged dye "S⁺" and negatively charged TiO₂ particle "e⁻".The electron injection takes place through the carboxylate-titanium linkage [Gre-2004]. The rate constants for charge injection and iodide reduction are at least 10⁷-10⁸ times faster than the degradation pathways as per mentioned previously at the end of chapter 1. This, in principle should guarantee a turnover of about 10⁷ without significant degradation of the dye [Spa-1997].

2.5 DSC standard assembling process and costs related

The sensitization of the nano-porous coating of TiO_2 is achieved by immersion within the dye solution. The counter electrode is deposited parallel to the photo-anode. They are separated by a spacer with a well defined thickness. Then, the solution containing the electrolyte redox mixture within a non volatile organic solvent is injected in between the electrodes. The injected mediator so far is naturally the (I^-/I_3^-) due to the corresponding high rate of conversion. The assembling is completed by a simple sealing. No high tech method is required and hence the fabrication costs are low. A typical DSC nano- TiO_2 based cell colored by Ruthenium complex 1 and functioning with the I^-/I_3^- as a mediator converts an AM 1.5 solar radiation flux with a rate of conversion of about 10% as indicated in Figure 15. This value, close to the ones obtained with photovoltaic cells is attractive if one considers the related costs. In terms of cost, the current price of titanium dioxide for which the annual world production is about 1 million of tons is of the order of 1\$/Kg. The nano-structured TiO_2 porous film within a DSC requires 18g/m^2 for a film thickness of about $10\text{ }\mu\text{m}$. The Ruthenium is in opposite costly but its usage is very limited and do correspond to an average cost of $0.07\text{\$/m}^2$. The TCO coatings onto the working electrode and the counter electrode count for about 14% of the total cost. In addition to the attractive cost effectiveness, the DSC cells could be used in different areas depending on the required rate of conversion and the spectral range of usage. The thickness of the porous nano- TiO_2 controls the amount of absorbed light and thus the photo-generated electrons. Typically, a nano-porous film of $10\text{ }\mu\text{m}$ and $0.3\text{ }\mu\text{m}$ allow a full absorption of 100% and 5% respectively with even a possibility of color design depending on the nature of the dye complex. As confirmed by Gratzel's team at the EPFL-Lausanne, the maximum voltage obtained depends on the oxyreduction potential of the mediator in the electrolyte solution. As mentioned previously, the best current candidate is the iodine-triiodine couple.

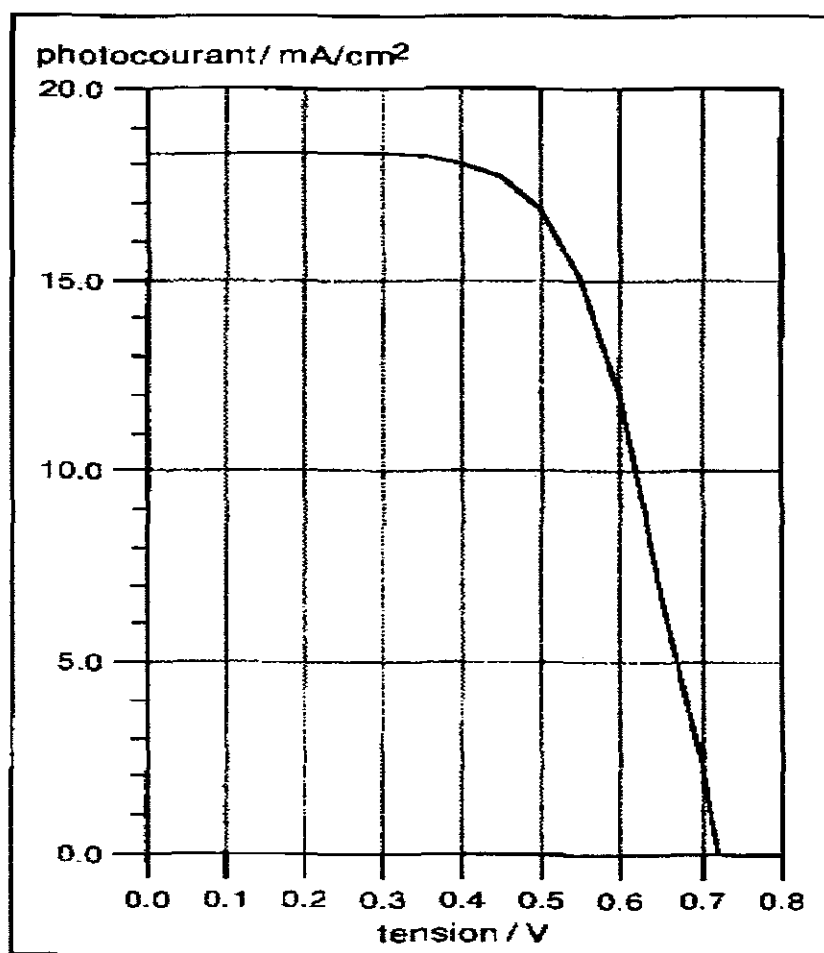


Figure 15: Photocurrent-voltage characteristics of nc-DSC [Mur-1995].

CHAPTER 3

3. TiO₂ PROPERTIES

3.1 Key properties of bulk TiO₂

TiO₂ is an n-type semiconducting oxide with valence and conduction bands mainly having O_{2p} and Ti_{3d} characters, respectively. Point defects such as oxygen vacancies give rise to extra electrons filling band gap states [Gre-2004]. It is acknowledged in the literature that titanium oxide exhibits several stable oxidation states including, Ti^{4+,3+,2+}, and the extra electrons as well as band gap states are being interrupted as one or two electrons occupying a metal site, i.e. in the upper half of the band gap therefore reducing the initial Ti⁴⁺ state. In general, bulk TiO₂ is found to be n-type due to the oxygen deficiency. TiO₂ exists in nature in three crystalline forms: rutile, anatase and brookite as it will be discussed later. As both anatase and rutile are the most frequently used forms, the survey conducted within this chapter will focus of both forms while Brookite form will not be discussed thoroughly. However, one should mention that the brookite is found to be present at high pressures and high temperatures. TiO₆ octahedra are interconnected differently for each phase, resulting to different structures and symmetries. Some of these crystalline varieties of TiO₂ are known to be metastable such as the cotunite whereas others are thermodynamically stable. Indeed, the volume of free energy of metastable forms is known to be always larger than those of stable phases. Rutile has been reported as a thermodynamically the most stable, most compact phase dominantly formed at high temperatures. It exhibits the highest refractive index of about 2.903 whereas anatase exhibit only 2.49. However, anatase is known to have a higher bandgap of 3.2 eV than that of rutile 3.0 eV. Furthermore, rutile on the other hand absorbs light in the near UV region band gap excitations lead to generation of holes, and this causes long term stability of the solar cell [Hal-2002]. The average values for cut-off

wavelengths and corresponding band gap energy for bulk TiO_2 are 388nm (3.2 eV) for anatase while 413nm (3.0 eV) for rutile. On the other hand, Anatase is known to be the most open structure being 10% less than rutile. Its structure is obtained at low temperatures around 350°C, which is useful for industrial applications. Anatase has been the dominant phase in study of dye solar cells since it is the primary crystal formed in the usual colloidal preparation method of the microstructural TiO_2 electrodes [Cac-2002]. However recent studies revealed that dye-sensitized nanostructured TiO_2 electrodes with pure rutile structure exhibited only 30% smaller shorter circuit photocurrent than pure anatase films and practically equal open circuit photovoltages [Hal-2002]. In this work, Anatase has been chosen for preparation of high density arrays of nanocrystalline TiO_2 for dye solar cell applications.

3.2 Redox power of semiconductors and choice of TiO_2

As discussed in the previous introductory chapters, nano-scaled TiO_2 is the semiconductor of choice in the dye solar cell technology in addition to its multifunctionalities. Nano-scaled TiO_2 is the most frequently used in the photocatalysis due to its well established photo-degradation activity for numerous pollutant gases, in addition of its biocompatibility, non toxicity, chemical stability and cost effectiveness. TiO_2 belongs to the transition metal oxides family. It is produced at the industrial scale as early as the 20th century as a pigment for white painting in replacement of lead oxide which is very toxic. Its annual production is estimated to be over 4 millions tones/year. TiO_2 has a large band gap comparable to zinc oxide as indicated in Figure 16. To justify the preference of TiO_2 within the Gratzel technology, one should shed light the essential aspect of photo-potential properties of such an oxide and its electrolytic compatibility as per schematized in Figure 16. It is well known that the solar cell photopotential is sensitive to the nature of the semiconductor surface that specifically determines the occurrence of recombination "i.e reverse reactions" [Gon-1996, Hal-2002, Goe-2003, Gre-2004]. The bandgap of TiO_2 is wide, about 3.0-3.2 eV depending on its crystalline phase structure. In connection with the energy band structure in particular, it is sensible to recall the relationship between the redox power of semiconducting oxides and their photo-generation properties. Semiconductors are capable of absorbing light with energy higher than certain energy threshold that is determined by the band gap, E_g of semiconductors. Photoelectrons and photoholes are generated once photons are being absorbed. The photogenerated electrons and holes relax to the bottom of the conduction band and to the top of the valence band respectively, by dissipating their kinetic energy. However, these electrons and holes can be therefore utilized to drive a redox reaction. From thermodynamics point of view, the energy levels of the conduction band edge " E_{cs} " is a measure of the reduction strength of electrons in the

semiconductor while valence band edge "E_{vs}" is a measure of the oxidation power of holes in the semiconductor. Figure 16 clearly illustrates the band edge energy levels of semiconductors that are in contact with aqueous media at pH= 0.0 [Jia-2004]. The higher the valence band edge potential, the higher the oxidizing power its holes have. Hence and accordingly to Figure 16, TiO₂ is the suitable candidate.

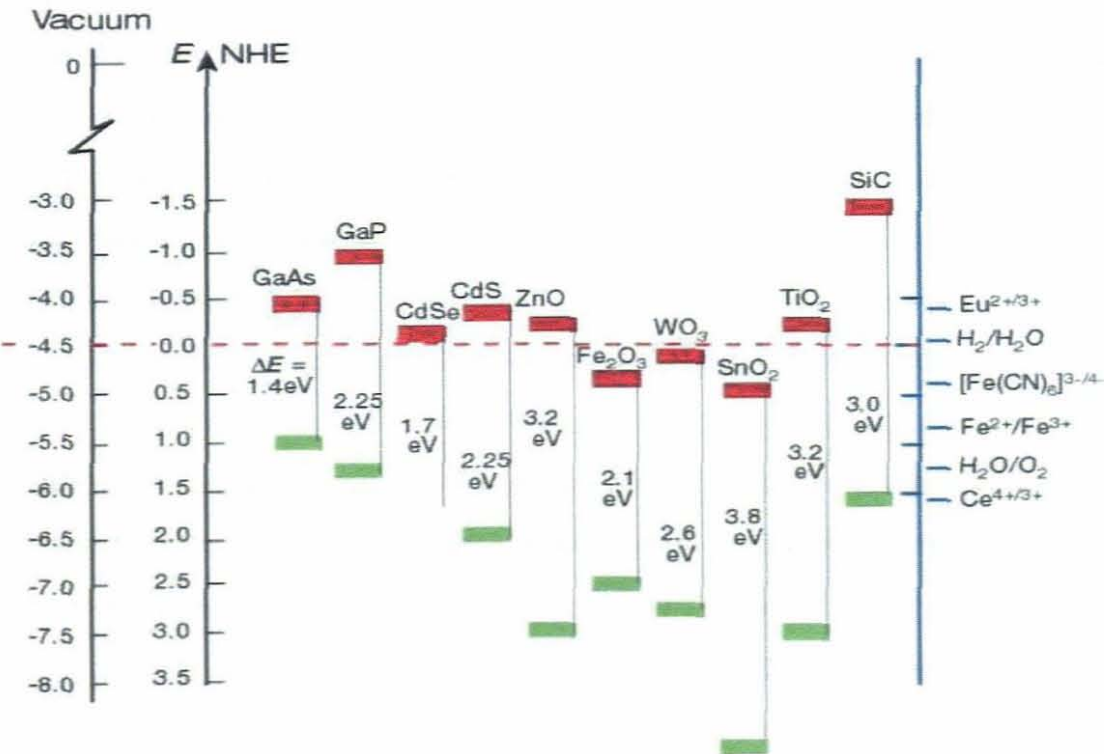


Figure 16: Energy-level diagram for various semiconductors indicating the energy positions of valence band and conduction band edges in aqueous media at pH 0.0 [Jia-2004].

3.3 Structural and crystallographic properties of TiO₂

As mentioned previously, in its bulk form, TiO₂ crystallizes in three allotropic crystalline forms: rutile, anatase and brookite as shown in Figure 17. Anatase (tetragonal structure) and rutile (tetragonal structure) are the most frequently found forms, in addition to the brookite (orthorhombic structure). The coordination pattern of each crystal phase is VI-III, but the Ti-O₆ octahedra share different numbers of edges [Table 2]. One should mention that there are two other forms synthesized at high pressure from the rutile structure. These are TiO₂ (II) and TiO₂ (H) which do possess PbO₂ and hollandite crystalline structures respectively. The three major TiO₂ crystal phases are considered to be commonly described as constituted by different arrangements of the same building block: a TiO₆ group where the titanium atom sits in the centre and is surrounded by six oxygens [Can-2003, Ran-2005]. The coordination pattern of each crystal phase is VI-III, but the Ti-O₆ octahedra share different of edges as shown in Figures 17. Each Titanium atom is in an octahedral of six oxygens and each oxygen is located within the triangle of three titanium atoms. The conventional primitive cells of anatase and rutile are also shown on Figure 17. In both structures, six atoms per unit cell are indicated and all atoms of the same element are equivalent by symmetry. Since anatase is a body-centred structure, so the represented conventional cell consists of two unit cells "12 atoms". In regards to the standard parameters a and b/c of the tetragonal Bravais lattice, an internal parameter u is required to fully determine the two structures. This parameter plays a significant role on describing the relative positions of the oxygen and titanium atoms. That is when a titanium atom is located at the origin, its apical oxygen atoms are located at $(0, 0, \pm uc)$ and $(\pm ua, \pm ua, 0)$ with apical Ti-O distance ua and $\sqrt{2}ua$ for anatase and rutile, respectively [Can-2003]. The atoms locations in the unit cell are

shown at Table 3; about 60% for (110) and of the order of 20% for (100) and (101) [Jon-1971].

The (110) face corresponds to the cleaving plan of the rutile and therefore the most abundant in natural rutile crystals. This face is composed upon 3 oxygen families as indicated in Figure 18. They consist of tri-coordinated O, bridging and terminal oxygens following the [001] direction in addition to the unique type of 6 coordination Ti atoms. One could notice that the bridging O-O distance is identical to the interdistance between the 6 coordinated Ti atoms. This distance is about 2.96Å. The same remark is valid following the [110] with a distance of 6.50Å [Cac-2002]. In its nano-scaled form TiO₂ exhibits a size depending structure with a phase diagram different from the bulk as sustained by numerous high pressure-high temperature investigations. The size dependence is mainly driven by surface tension and Gibbs surface free energy. If the rutile phase is the high temperature stable structure, the anatase is the primarily obtained phase by soft physical-chemical process. The anatase is the primarily stabilized phase in nano-materials. Banfield et al [Zha-2000] have studied the stability of diverse polymorph phases of TiO₂ by X-ray diffraction during isochrone and isotherm treatments. The obtained results clearly indicated that for nano-particles' size smaller than 11nm, the anatase phase is stable while the brookite phase is stabilized in the range of 11-35nm. Above 35 nm, the rutile is the established phase. Regarding the anatase-rutile phase transition, the threshold size determined by the above mentioned X-ray diffraction is estimated to 16nm while the theoretical value was estimated to 14 nm [Zha-1998]. Barnard et al [Bar-2005] have established by modeling that the critical phase size anatase-rutile phase transition depends upon the surface state of the nano-crystals. The H₂O surface adsorption on anatase enhances its stability relatively to the phase rutile. In this hydrated state, the anatase phase is stable for size as higher as 15nm while it is about 9.6 nm for

un-hydrated state. A similar study has confirmed the influence of the surface in acidic or basic conditions on the phase transition threshold. To represent acidic conditions, the TiO_2 surface is saturated by hydrogen atoms i.e. all under-coordinated sites are terminated by a hydrogen atom. A neutral surface corresponds to water adsorption while for basic conditions, the under-coordinated Ti atoms are terminated with O atoms [A Bar-2005]. Acidic are conditions, stable is the anatase phase. The anatase/rutile phase transition takes place at about 22.7 nm in size for an acidic surface while for a basic surface it is about 7nm [A Ba-2005].

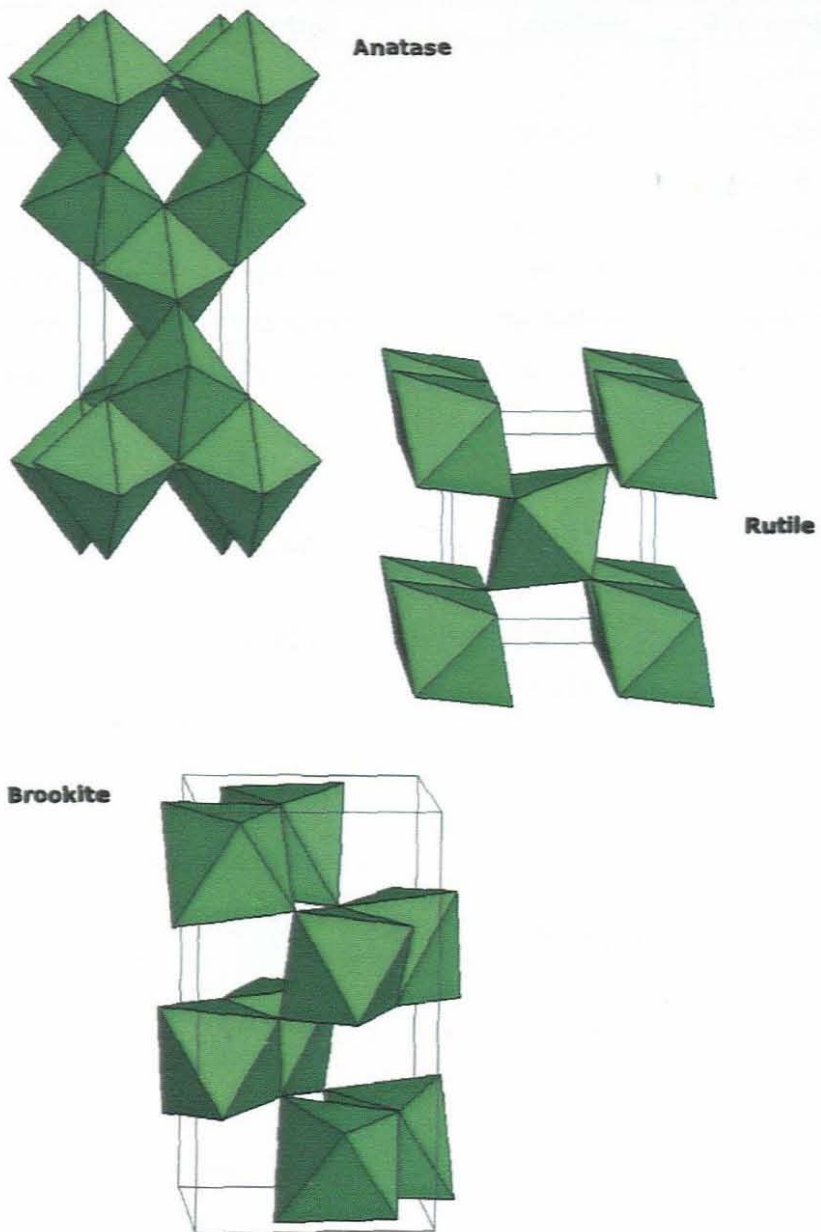


Figure 17: Different crystalline forms of bulk TiO_2 : (a) anatase, (b) rutile and (c) brookite.

Table 2: Crystallographic properties of TiO₂ phases

	Rutile	Anatase	Brookite
Molar Weight	79.890	79.890	79.890
Z	2	4	8
Density "g/cm ³ "	4.26	3.8	4.123
Molar Volume	18.693	20.156	19.377
Bravais lattice	tetragonal	tetragonal	orthorhombic
Space group	<i>P4₂/mm</i>	<i>I4₁/amd</i>	<i>P/bca</i>
Sym.Ti	<i>D_{2h}</i>	<i>D_{2d}</i>	<i>C₁</i>
Sym.O	<i>C_{2v}</i>	<i>C_{2v}</i>	<i>C₁</i>
a "Å"	4.584	3.785	5.456
b "Å"			9.182
c "Å"	2.953	9.514	5.143
V "Å ³ "	62.07	136.25	257.28

Table 3: Atoms locations in the unit cell.

	Rutile	Anatase
Ti 1	(0,0,0)	(0,0,0)
Ti 2	(a/2,a/2,c/2)	(0,a/2,c/4)
O 1	(-ua,-ua,0)	(0,0,-uc)
O 2	(+ua,+ua,0)	(0,0,+uc)
O 3	(a/2-ua,a/2+ua,c/a)	(0,a/2,c/4-uc)
O 4	(a/2+ua,a/2-ua,c/2)	(0,a/2,c/4+uc)

3.4 Electronic properties of TiO₂ and size effects

TiO₂ is known to be the strongly ionic material composed of Ti⁴⁺ cations and O²⁻ anions. Therefore, the filled valence band is composed of the outermost p electrons of Oxygen whereas the lowest conduction band mainly derived from titanium 3d orbitals. It is also believed that, when some Titanium atoms are exposed in the surface regions of nanoparticles and changed into Ti³⁺, Ti²⁺ and Ti⁺, localized energy levels are introduced within the forbidden gap [W Zha-2000]. Recent reports revealed that, two 3d electrons of the isolated titanium atom are not completely transferred to oxygen in the solid where they contribute to the formation of a partially covalent bonding [Can-2003]. This method is believed to be an essential condition for ferro-electricity. TiO₂ can be regarded as an incipient ferroelectric material. Even if it does not undergo a ferroelectric phase transition, it is still characterized by a very large electric polarization [Can-2003]. Researchers reported on their experimental work that in both rutile and anatase, there is a significant contribution from Ti-3d states "13.8% and 13.9%" of the total muffin-tin contribution to the top valence band states of rutile and anatase, respectively. However, the topmost of valence bands include the 12 bands arising mainly from Oxygen 2p and Ti 3d states "the O-2p bands". Whereas the lowest lying conduction bands have predominantly Ti-3d character and indeed, they are separated in two non-overlapping sets, t_{2g} and e_g related to the splitting of the atomic Ti-3d states in an octahedral coordination environment [Can-2003]. Naturally, this electronic difference corroborates with different optical properties of the two phases. More specifically, the difference in dielectric functions of Anatase and rutile is the optical anisotropy near the absorption edge which appears to be much stronger in anatase than in rutile. In addition, experimental investigations of the optical absorption edge for anatase single crystal found in literature indicated that anatase has larger dichroism edge

than rutile, the oscillator strength of the transition near the absorption edge for perpendicular polarization is one order of magnitude larger than that for parallel polarization and it is therefore concluded that the excitons in anatase are self-trapped while those in rutile are free.

In addition to the net difference between nano-scaled and bulk TiO_2 in terms of surface/volume ratio and structural properties, the size of the semiconducting TiO_2 particles would affect their electronic properties as well [Kar-2002]. As for the size dependence of the crystallographic structure which is driven by surface tension parameters, the difference can be described by the potential distribution at the interface on the semiconductor side. In order to derive this potential distribution, linearized Poisson-Boltzmann equation can be used. The potential distance between a distance r and the centre of the TiO_2 semiconductor particle ' $r=0$ ' can be expressed as [Figure 18]:

$$\Delta\Phi_{sc} = \frac{kT}{6e} \left(\frac{r - (r_0 - W)}{L_D} \right)^2 \left(1 + \frac{2(r_0 - W)}{r} \right)$$

where $\Delta\Phi_{sc}$ is the potential drop within the layer, k is the Boltzman constant, r represent the distance starting from the of the particle, T denote the temperature, e is the electronic charge, N_D represents the dopant concentration, $L_D = (\epsilon_0 \epsilon k T / 2e^2 N_D)^{1/2}$ represents the Debye length depending on the dopant concentration and on the charge carrier, W is the of the space charge layer, ϵ_0 is the permittivity of the vacuum and ϵ denotes the dielectric constant of the TiO_2 semiconducting particle.

In the case of the bulk semiconductor, the potential drop within the particles can be expressed by:

$$\Delta\Phi = \frac{kT}{2e} \left(\frac{W}{L_D} \right)^2$$

whereas in the case of TiO₂ nanoparticle semiconductor, the potential drop within the nanoparticle is expressed as:

$$\Delta\Phi = \frac{kT}{6e} \left(\frac{r_0}{L_D} \right)^2$$

The above equation indicates that the potential drop within the TiO₂ semiconductor nanoparticles is very small because of the small value of r_0 . This therefore makes the semiconducting nano-particle to behave completely different from the bulk. In other words, this suggests that the bands within the semiconductor are almost quasi-flat as illustrated in Figure 18 [Gon-1996]. The charge separation occurring within the particle via an electron diffusion mechanism is believed to be due to the small band bending. However, the electron-hole pairs generated during light absorption are spatially randomly distributed along the optical path. In fact, based on the random walk model, the average transit time of electrons for semiconducting nanoparticles from the inside of the particles to its surface is in order of picoseconds [Jia-2004]. Such a diffusion process is faster than the electron/hole recombination process, but since the photoelectrons and photoholes are still so close the charge separation issue has not yet been resolved.

Nanoporous semiconductors are known to belong to the kind of materials with extremely low drift mobilities " μ " of charge carriers because of the complex network of a nanoporous structure and also the huge internal surface area of a porous semiconductor which may lead to hopping transport on a fractal or trap limited

transport [Dit-2000]. For an example, for electrons in nanoporous Si and TiO₂, μ is in order of 10^{-4} - 10^{-1} and 10^{-4} - 10^{-6} cm²/Vs, respectively which is lower by four to six order of magnitude than μ for the single crystalline Si and TiO₂.

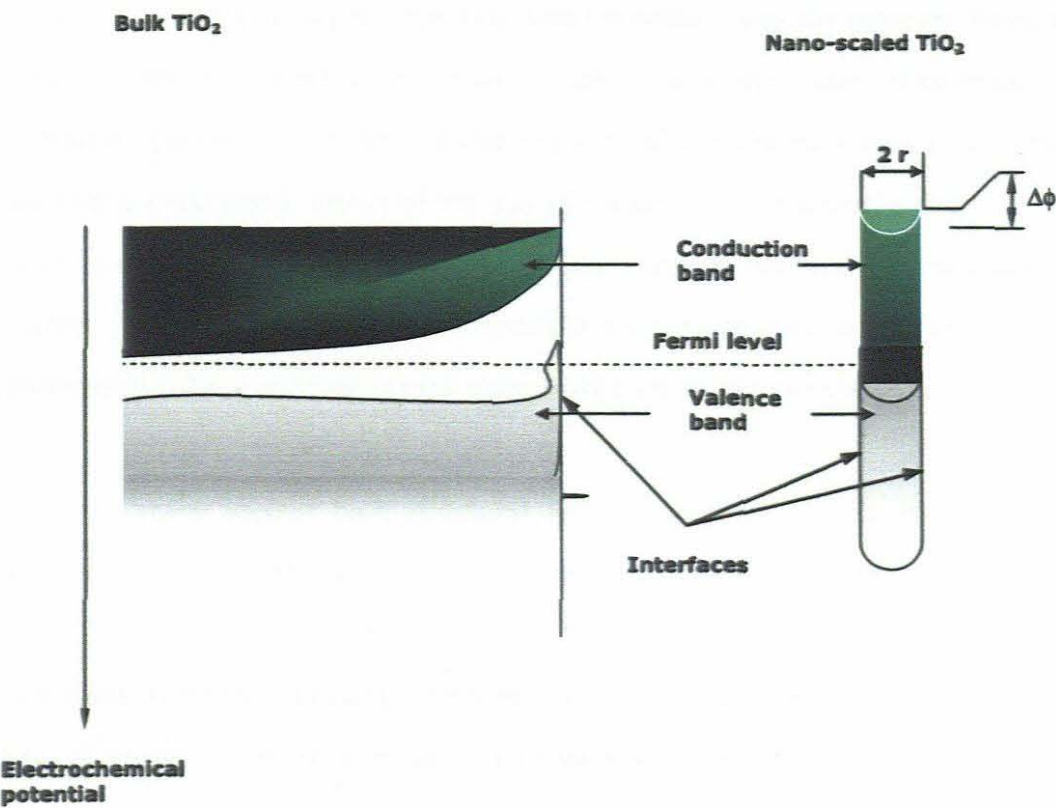


Figure 18: Diagram indicating the difference of band bending at semiconductor solution interface between n-type bulk semiconductor and nanoparticle semiconductor.

3.4 Surface atomic ordering of TiO₂

Attempts to improve the efficiency of the TiO₂ based dye-sensitized semiconductor electrodes are closely linked to some of the most important current developments in molecular science. As mentioned previously, in particular, the TiO₂ semiconductor electrodes used are prototype nanostructured materials, and the initial charge-separation process across the dye-TiO₂ semiconductor electrode contains interesting aspects both of ultra-fast chemical dynamics and molecular electronics. The interaction between dye molecules and Titanium oxide surfaces is thus an important, but poorly understood, aspect of the dye-sensitized electrochemical devices. While a good contact (molecular anchoring) of the dye molecule onto the TiO₂ nanoparticles surface [Figure 19] is crucial for the performance of the devices, the interaction is particularly difficult to study, as the components are highly complex.

Recently, many studies both structural and spectroscopic effects involved in the adsorption of the dyes on the TiO₂ nanoparticles' surfaces have been achieved and realistic models were proposed. From the computational point-of-view, the central processes in artificial photosynthesis are very similar to those in the Grätzel solar cell. A common feature of these interfacial electron transfer systems is that the complexity of the systems in the past largely has prevented theoretical studies by means of accurate quantum-chemical calculations. With increasing possibilities to perform calculations that capture the essential physics and chemistry of these systems, a significant effort to put this field on a firm theoretical basis would be timely. Ultra-fast surface electron transfer from aromatic and organometallic dyes to wide band-gap metal oxides including TiO₂ is an intriguing feature in many of the systems currently under intense experimental investigation. The present understanding of these electron transfer reactions, via the dye- TiO₂ nanoparticle

interface, is, however, much poorer than e.g. electron transfer in solution. Ab initio quantum-chemical calculations will play an important part in the formulation of accurate models for these electron transfer reactions in the coming years. The quantum-chemical calculations have the potential to provide essential information on several aspects of the interfacial dye-TiO₂ interactions. So far, it is expected that the dye-TiO₂ nanoparticles' interface would play a critical role for the overall rate of conversion [Per-2002, Nil-2006, Lun-2006]. Firstly, these interface phenomena could establish a molecular view of the adsorption geometry. Secondly, they could allow a detailed view of the electronic structure as in cases of strong surface-adsorbate interactions where the conventional view that the adsorbate states are essentially unaffected by the TiO₂ substrate breaks down. Thirdly, this would permit to interpret electron transfer processes in terms of the calculated electronic states. Consequentially, a survey of allowed TiO₂ surfaces is required. A series of the major surface cleavages of TiO₂ are given below. This atomic faceting depends on the crystalline phase.

It is noticed experimentally that the (110) face is the most stable face for rutile. Likewise, it is proven from theoretical point of view that the (110) is favorable energetically than the (100) and (101) faces [Ram-1994, Lin-2001]. The distribution rate of the faces in polycrystalline powder is investigation of the (110) face. Atomic plans of 3.2 Å in thickness were observed by Scanning Tunneling Microscopy following a surface treatment by ablation and a heat treatment at 1100K under ultra-high vacuum [Uet-2000]. Other authors have determined by Scanning Tunneling Microscopy also an average distance of about 6.3 Å between the bridging oxygen atomic chains in agreement with the crystallographic values of the elementary cell [Die-1998].

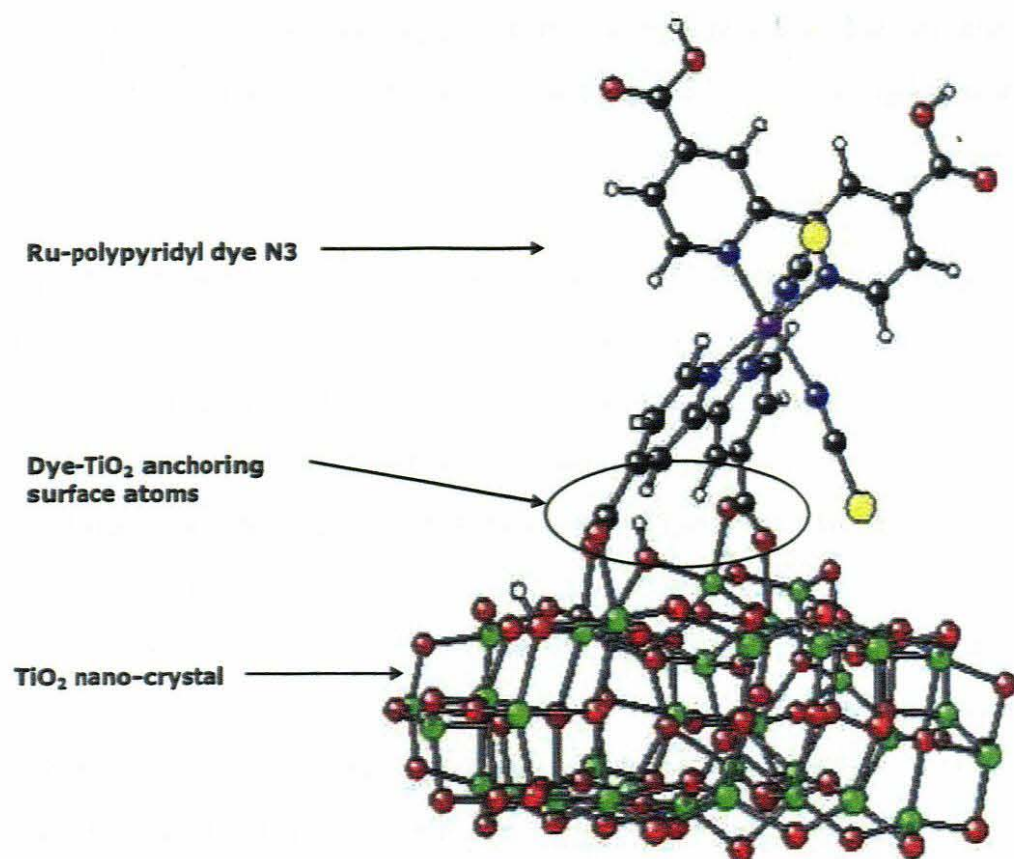


Figure 19: Density functional theory optimized geometry of the Ru-polypyridyl dye N3 on a TiO₂ nanocrystal [Per-2002].

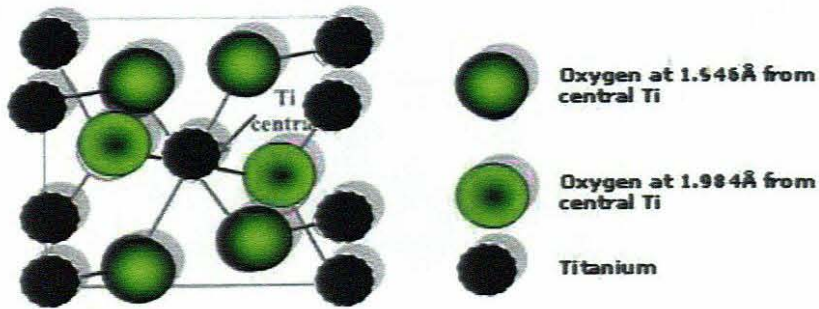
It is mentioned in the literature that an atomic relaxation phenomenon takes place at the surface and therefore a reconstruction of the TiO_2 . Indeed, for the relaxation phenomena, the Ti and O surface atoms without their full co-ordinations minimize the Ti-O neighboring distances. The surface X-ray diffraction under grazing incidence indicates that the distance separating the surface bridging O atoms and the Ti surface atoms diminishes by 0.3 Å for an initial value of 1.95 Å as indicated in Figure 20 [Cha-1997].

The (001) rutile face presents an atomic layering completely different from the (110) face. Moreover, this surface face is the least studied one because it is the least thermodynamically stable face according to the ab initio calculations [Ram-1994]. Nonetheless, microcrystals with such a faceting were obtained which alludes to the existence of atomic reconstructions stabilizing the (001) faceting. This (001) faceting comprises two Ti families with 5 and 6 co-ordinations as well as two O families (terminal and bridging O chains) within the [100] direction. The (001) face of the rutile phase can be decomposed in elementary squared units with an identical distance between 2 neighboring oxygens and titaniums within the [100] and [010] directions. As for the (110) face, the atomic force microscopy study showed the existence of terraces of 3 Å at the surface of the (001) face [Ter-2003].

The (111) crystalline face of the rutile structure is the least studied face. The unique viable information in the literature is that numerous atomic reconstructions are possible depending on the heating temperature [Uet-2000]. It can be described by a homogeneous representation such as the (001) face which possesses a similar atomic rearrangement. It exhibits therefore Ti atoms 6 times coordinated and 1 type of bridging O atoms within the [011] direction. The distance between Ti and O atoms is of 5.46 Å. Similarly to the (001) face, the surface can be decomposed to

elementary units exhibiting a parallelogram form. The (100) and the (101) faces of the rutile structure are not well understood as their atomic arrangements involve numerous unclear reconstruction phenomena. For the (100) face, quantum chemical calculations have established the existence of a significant atomic rearrangements at the surface taking into account both oxygen deficiencies as well as different type of surface relaxations [Lin-2001]. The anatase phase is an allotropic form of TiO_2 which was extensively investigated. Indeed, monocrystals of anatase are difficult to synthesize with the same processes used for the production of rutile monocrystals. According to the literature, there are contradicting results about the stability of the stable phases [Con-1996, Sck-1997, Vit-1998, Fin-2001]. If there is a consensus about the rutile stable faces, those of the anatase form are still discussed. The bulk of the literature indicates that the different methods of synthesis produce anatase with mainly (100) and (101) faceting with a smaller proportion of (001) faceting [Had-1996, Vit-1998]. Other authors consider the natural cleaving faceting, essentially (001) [Pri-1971]. Concerning this anatase (001) faceting, and as for the rutile phase, the surface is presented as hydrolyzed (see figure 21). Therefore it exhibits one type of Ti atoms and 2 types of O atoms. While the Ti atoms are 6 time coordinated and the O ones are of bridging and terminal types. Hence, the representation of each crystalline face will be coherent respecting a homogeneous surface hydroxylation. Concerning the anatase (101) and (100) faces, the minimization calculus of the surface energy in the literature has allowed concluding that the (101) is the most stable crystalline face [Laz-2000]. More precisely, the Scanning Tunneling Microscopy indicate that this face consist of 2 Ti atoms family, 5 and 6 co-ordinations with two O atoms type, 3 co-ordinations and bridging type [Hed-2000].

(a)



(b)

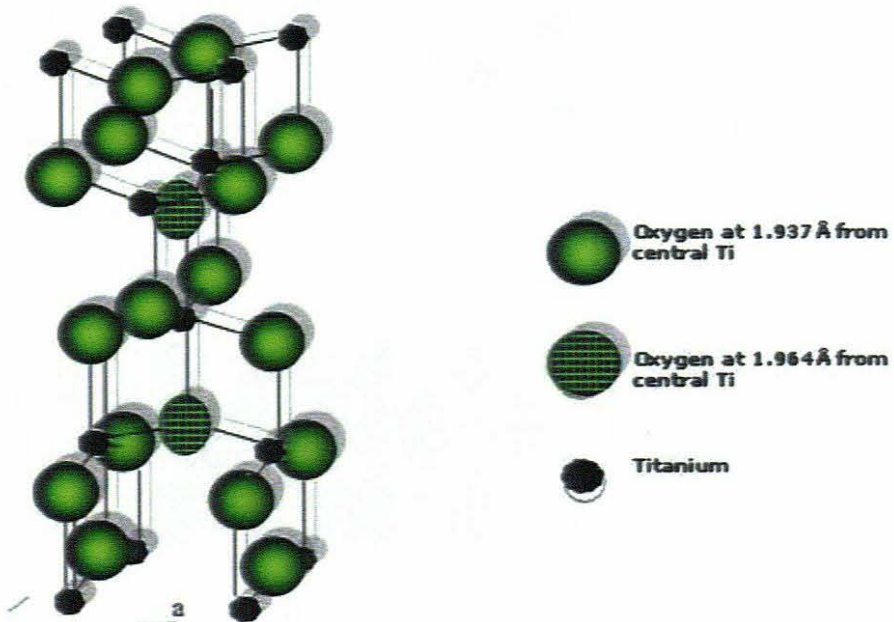


Figure 20: Atomic sites of Ti and O in the elementary cell of (a) rutile and (b) anatase phases.

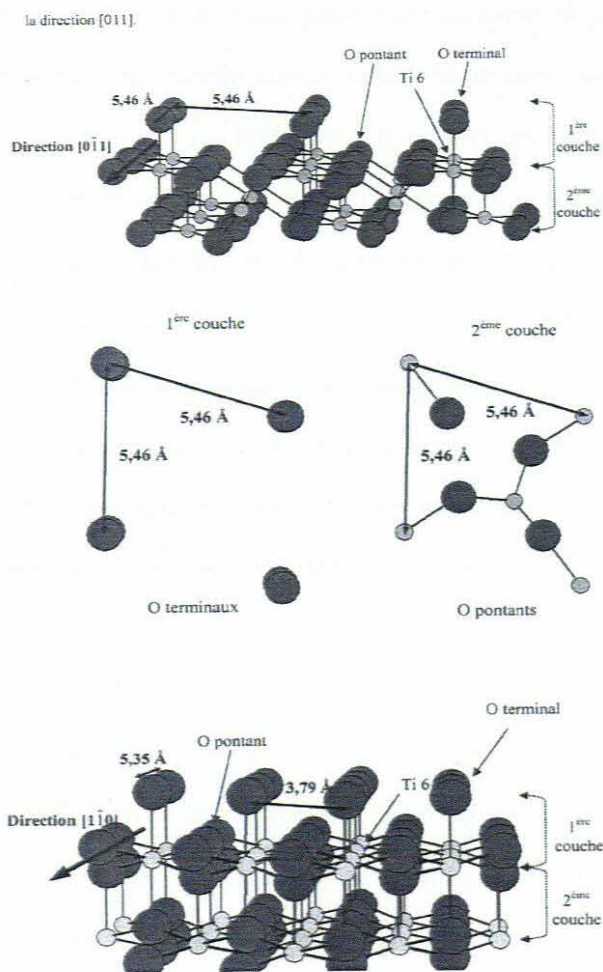


Figure 21: Face (001) of the rutile phase; projections on the 001 plan [Per-2002].

CHAPTER 4

4. LITURATURE REVIEW

4.1 Evaporation induced self assembly (EISA)

The template method, where inorganic intermediate oligomers polycondense in the presence of surfactant micelle super-molecular arrays, was first discovered by Mobil for silica based materials in 1992 [Bec-1992] and since then it has been used for the preparation of *meso-structured and meso-porous materials using various networks and templates* as reported by Brinker et al [Bri-2003]. Among the pioneering materials to be synthesized, mesoporous silica has been extensively used and the most studied one. The technique is nowadays well known as the Evaporation Induced Self Assembly process or EISA. Due to its simplicity and large surface coating capabilities, this evaporation induced self assembly used nowadays in engineering nano-materials to form ordered structures promises novel opportunities for the development of miniaturized electronic, optoelectronic and magnetic devices [Thu-2000, Whit-2002, Tsu-2004, H Ko-2006]. In this regard, even if several novel elegant methods based on self-assembly have emerged recently [Lin-2005, Gle-2005, Hua-2005, Kal-2006], the evaporation induced self assembly is currently the most used even if the electrostatic self-assembly [Kal-2006] is competitive. Self-assembly of nano-particles by irreversible solvent evaporation has been recognized as a very competitive and simple route for the synthesis of highly ordered and complex structures [Dee-1997, Dee-2000, Rab-2003, Big-2006].

Evaporation induced self-assembly process is a more advanced synthetic procedure which allows for the turning of the inorganic condensation rate with the formation of an organized liquid-crystal template. The surfactant templated mesoporous materials synthesized by the EISA methodology have been demonstrated to exhibit unique

structures and properties, including uni-modal pore size distributions, high surface areas, alterable pore sizes and controlled pore surface chemistry. The mesopores size range of 2 to 50 nm is interesting for producing confined structures such as quantum dots [Srd-1998, Hir-1999, Par-2000] or 1-D nano-systems such as nanowires [Han-2000, Hua-2000]. The significant uniform porosity of the mesoporous materials allows for facile diffusion, thereby making them attractive hosts for sensing molecules and ions [Yin-1999, Say-2001].

As illustrated in Figure 22, the traditional synthetic approach to these mesoporous materials by the EISA involves 4 major different phases. Phase 1 consists of mixing the inorganic precursor and the polymeric building blocks in the adequate proportions and chemical conditions. Phase 2 consists of the formation of a hybrid inorganic-organic ordered mesophase system following a sol-gel reaction phenomenon and removal of the organic solvents. This compact hybrid mesostructure is spontaneous self-assembly of amphiphilic molecules from the bulk solution, with concurrent templating of inorganic precursor species through electrostatic or hydrogen bonding interactions with the amphiphilic molecules. This ordered intermediate phase is a liquid crystalline mesophase like structure. The slow co-assembly of an organic network around so called liquid crystalline phase allows the formation of a well-defined mesostructured material. The initial acidic conditions which are subsequently eliminated by evaporation of the acid provide a means for readily controlling the polymerization of the inorganic network. Phase 3 comprises the obtention of a consolidated more rigid hybrid ordered mesostructure obtained following a mild aging treatment. The last phase, phase 4 is obtained by eliminating the polymeric template by calcinations generally. However, the stability of the inorganic network upon removal of the template is one of the difficulties in successfully synthesizing mesoporous transition-metal based materials.

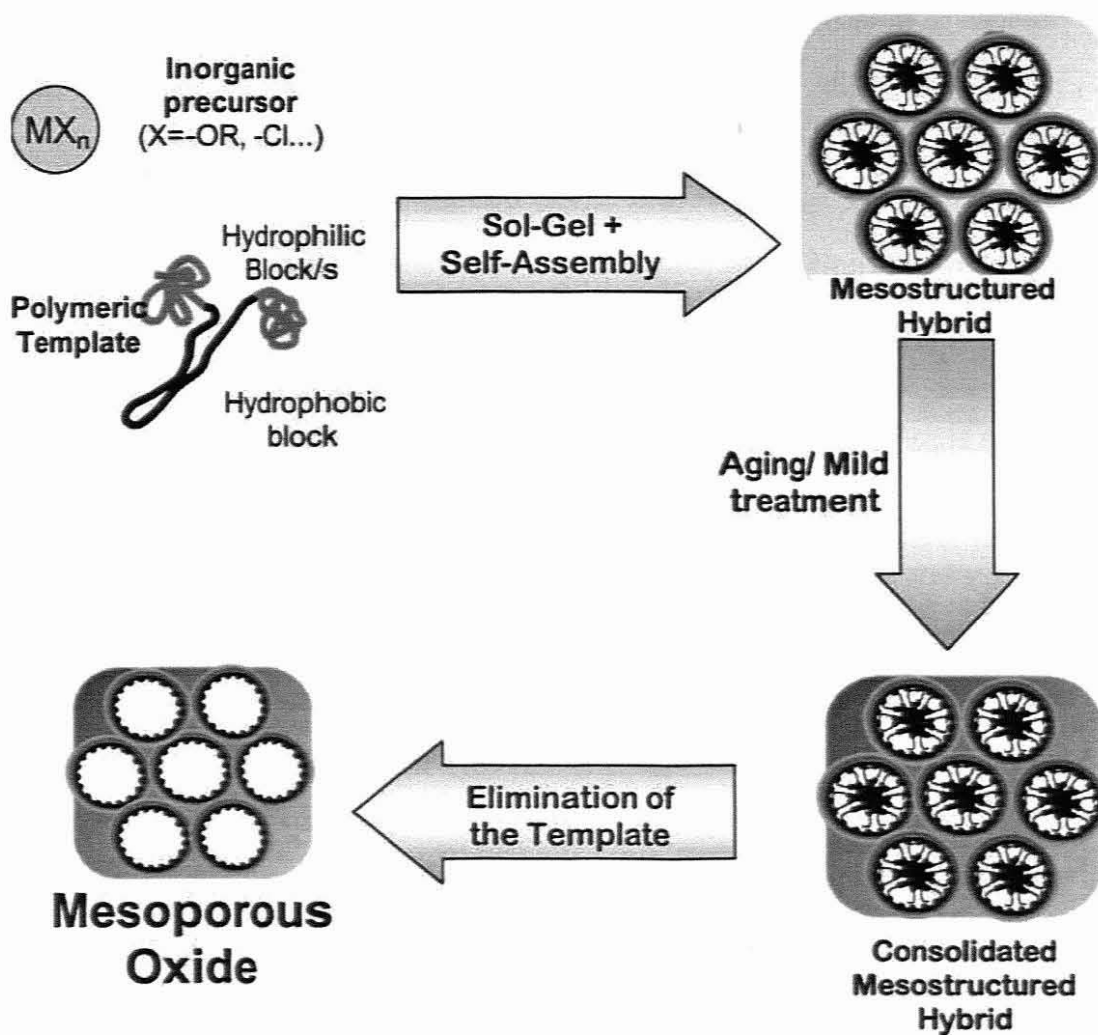


Figure 22: Four major steps that occur during evaporation induced self assembly.

Pore space can be liberated through the removal of the template by either thermal treatment "calcination" or repeated washing. Removal of template by washing can end up to complete dissolution of the material due to an insufficiently condensed inorganic framework. Calcination of the on the other hand is often unsuccessful, leading in poorly ordered materials or dense, fully collapsed structures. There are two most common reasons for instability of the mesostructures during calcination which are due to the modifications of the valence state of the transition metal via redox reaction or excessive crystallization/grain growth of the inorganic phase. Excluding these aspects of stability, the EISA allows an effortless way to control the shape and the ordering generated subsequent to the self assembly phenomenon. As reported in Figure 23, the isotropic, cubic, 2-D hexagonal and lamellar configurations depend on the temperature-surfactant concentration phase diagram. More importantly, this method is widely acknowledged in the literature as the interesting procedure for the synthesis of mesoporous transition-metal based materials with the above mentioned structural configurations since it uses a very dilute initial conditions from which a liquid crystalline mesophase is gradually formed upon solvent evaporation. Figure 24, reports typical structures of mesoporous WO_3 , CeO_2 , ITO, TiO_2 and ZrO_2 synthesized by using the KLE family as block co-polymers (KLE: (poly(ethylene-co-butylene)-block-poly(ethylene oxide)) and the standard Brij58[Bre-2006].

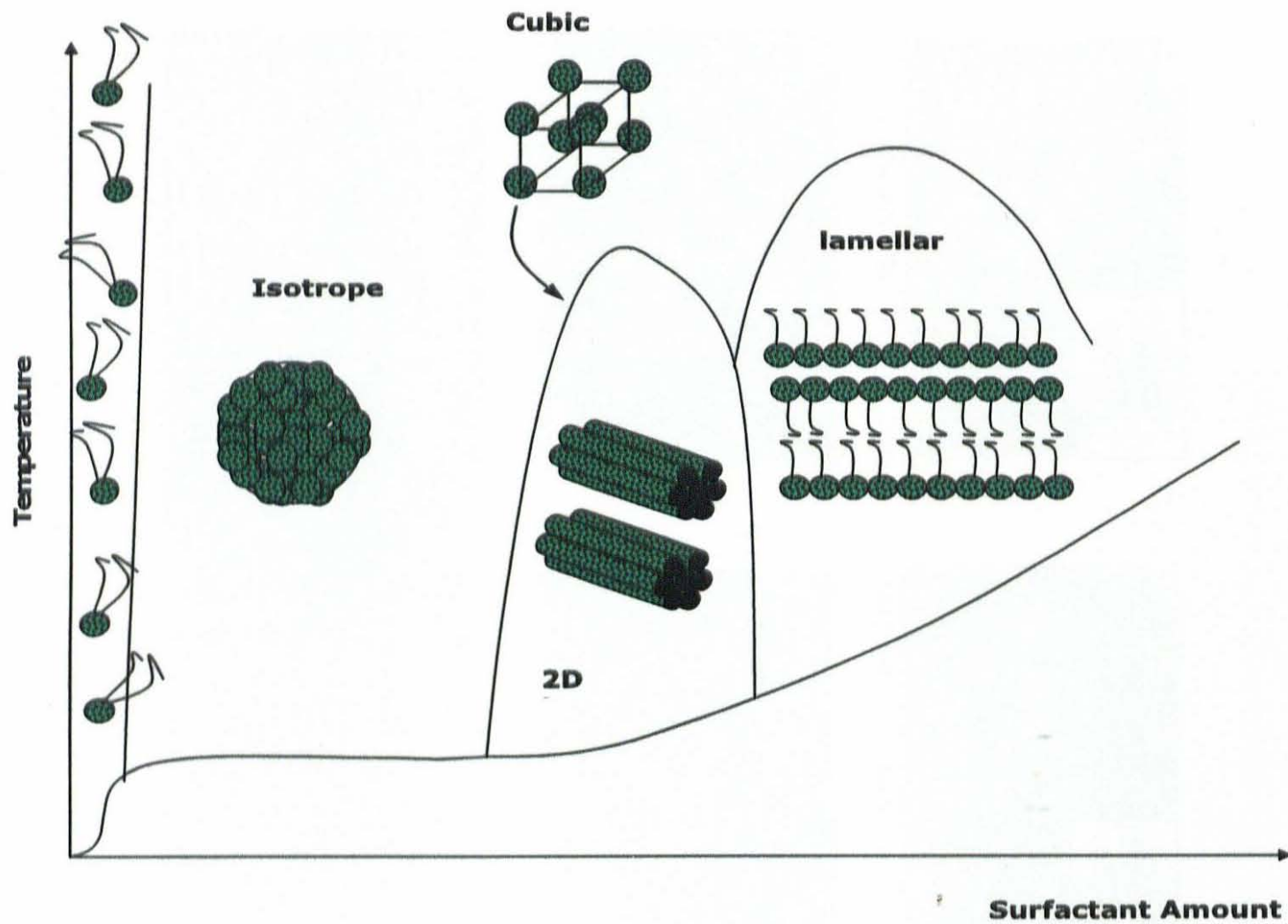


Figure 23: the isotropic, cubic, 2-D hexagonal and lamellar configurations depend on the temperature-surfactant concentration phase diagram.

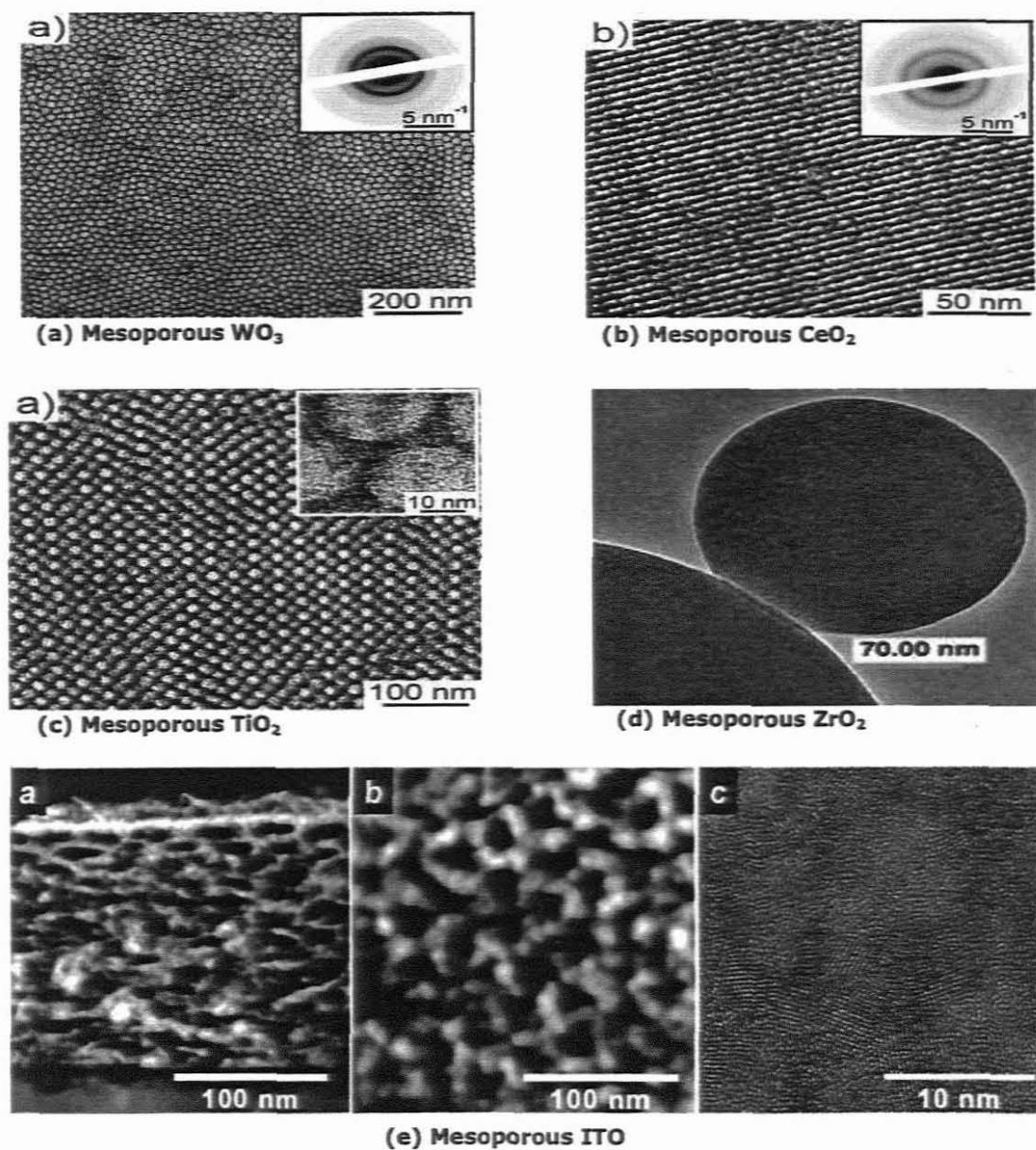


Figure 24: typical structures of mesoporous (a) WO_3 , (b) CeO_2 , (c) TiO_2 (d) ZrO_2 and (e) ITO synthesized by using the KLE family as block co-polymers and the standard Brij58 [Bre-2006].

4.1.1.1 Evaporation induced self assembly (EISA) of mesoporous TiO₂: survey.

Since mesoporous materials can be prepared by combining the sol-gel chemistry and the structuring effect of surfactants, they have attracted attention for application in various high technology fields. More specifically, extensive studies on mesoporous SiO₂ and TiO₂ by EISA were carried out in the literature among them, one should mention the corresponding recent studies in addition to the pioneering work of Brinker [Bri-2003]. In this section, the focus is on the TiO₂.

Hwang et al [Hwa-2006] have synthesized mesoporous titania thin films with distinctly interconnected pores in 3-D configuration with a pore size diameter of about 3nm using EISA method. The pores exhibited a pseudo-cubic structure derived from the *Pm3m* crystallographic configuration. By systematically studying the influence of the main synthesis parameters such as the humidity during the spin-coating and aging steps, composition and aging temperature, as well as aging time, they have established optimal conditions for reproducible synthesis of pseudo-cubic structured mesoporous titania thin films. The combination of the conventional TEM and XRD revealed that the pores spatial ordering within the films was highly regular without any defect in the scale of several hundred nanometers. In addition to the in volume quasi perfect 3-D ordering, the surface investigations by AFM showed that the film surface was very flat and exceptionally smooth with roughness less than 0.3nm. Electrochemical analysis of several analyte molecules of different sizes on Pt electrodes with and without the mesoporous titania film coatings clearly indicated that the as synthesized mesoporous titania thin films have exceptional size exclusion properties in the nanometer scale. In addition the combination of electrochemical deposition in aqueous solutions and using these titania thin films as a template, 3-D network of silver (Ag) nanoparticles' arrays have been successfully synthesized.

Zhao et al [L Zh-2004] used EISA to produce mesoporous titania film using nonionic triblock copolymer as surfactant template. The nonionic triblock copolymer as surfactant template was removed by ethanol extraction followed by calcinations a phase at about 400°C. The Grazing Incident-XRD and the TEM investigations matched with far infrared spectroscopy and Auger analysis substantiated the full removal of the surfactant by ethanol extraction and calcination whilst the films exhibited a higher ordered meso-structure. Moreover, the room temperature UV-VIS spectroscopy studies provided the evidence for coordination states existing between the titanium species and hydrophilic (PEO) moieties.

Using EISA as a synthesis approach, Liu et al [Liu-2005] have demonstrated the possibility to synthesize relatively very large pores mesoporous nanocrystalline titania thin films. In this case, the mesoporous nanocrystalline TiO_2 thin films with a large-pore diameter, as large as 14 nm with a significant narrow pore-size distribution have been synthesized by using tetrabutyl titanate as the inorganic precursor and triblock copolymer (Pluronic P123) as the structure-directing agent under acidic conditions. It was clearly demonstrated that the meso-pores' size of the as engineered samples can be adjusted/controlled by altering the inorganic source/surfactant mass ratio.

By EISA and in terms of micro-particles 3-D ordering, Fu et al [L Fu-2007] have succeeded recently the preparation of three-dimensionally ordered mesoporous titania microparticles as anode material for lithium ion battery. More accurately, free standing 3D ordered meso-porous anatase titania microparticles were prepared by using polystyrene colloidal crystals as a template as substantiated by TEM, XRD, Thermogravimetry and Electrochemical measurements. As anode materials for lithium ion battery, they present exceptional kinetic performances and good capacity retention due to their special architecture with mesoporous channels and thin walls

which are ideal to the lithium ions diffusion. Besides, mixing 3D ordered mesoporous titania microparticles with conductive additive can reduce the resistance of the anode, favor the mobility of the electrons, and decrease the polarization.

Soller et al [Sol-2002] have produced and investigated mesostructured TiO_2 -hexadecyltrimethylammonium bromide hybrid powders, displaying a bidimensional hexagonal pattern of $P6m$ crystallographic type in ethanol/HCl/ H_2O media by using EISA as a synthetic approach. Thermal treatment of these so called titaniatropic hybrid phases lead to phosphorus-free, high surface area within the range of 280-370 $\text{m}^2 \text{g}^{-1}$ mesoporous titania, with 2.0-2.5 nm pores. The role of the synthesis parameters such as surfactant and acid concentrations in addition to temperature was thoroughly discussed to understand their influence on the hybrid mesostructures. It was suggested that hydrophilic Ti-oxo nanometric building blocks formed in the acidic synthesis conditions self-assembly upon solvent evaporation are at the origin of the stability of such hybrid meso-porous composites.

Zhang et al [S Zh-2004] on the other hand have succeeded for the first time to produce multilayered systems using EISA. The ordered TiO_2 /Poly (DMCB) multilayered structures were prepared on glass substrates. In the multilayered thin films, the surfactant DMCB was used as both structure-directing agents and monomers. The results indicated that the films were composed of organic and inorganic layers with orderly interlaced arrangement and the interlayer distance between organic layer and inorganic layer was 7.17 and 6.26 nm before and after polymerization, respectively.

Doping using EISA is also possible, Fan et al [Fan-2008] have succeeded to synthesize phosphated mesoporous TiO_2 photocatalytic materials. The phosphated

mesoporous TiO_2 were synthesized by using phosphorus content from 1 to 15 mol%. The X-ray diffraction and N_2 adsorption–desorption isothermal results revealed that the incorporation of phosphorus was of benefit in improving the thermal stability and enhancing the surface area of mesoporous TiO_2 by constraining the growth of anatase crystallite. X-ray photoelectron spectroscopy confirmed that the phosphorus in the calcined phosphated samples exists as amorphous titanium phosphate in a pentavalent-oxidation state P^{5+} while embedded into the nanocrystalline anatase TiO_2 . In photodegradation gas phase acetaldehyde, the photocatalytic activity of the samples was higher than that of pure mesoporous TiO_2 and the standard Degussa P25.

By EISA and in terms of titanium isopropoxide based precursors, Kartini et al [Kar-2008] were the pioneers in using Ti isopropoxide precursors to engineer mesostructured Titania thin films. The highly acidic sol precursors contained Ti^{4+} tetraisopropoxide as a titanium source with a tri-block copolymer (Pluronic P123) as a template, and acetylacetonate and HCl as hydrolysis inhibitors. The morphological and crystallographic investigations by TEM and on the as-synthesised films revealed the appearance of cubic-like, pseudo-hexagonal, and lamellar mesophases; depending on the amount of water in the sols of film precursors. Template removal by a calcination process yields high surface area in the range of 320–360 m^2/g of mesoporous titania with crystalline anatase frameworks. Naturally, it was found that the water content influences the degree of anatase crystallinity of the final calcined films. More precisely, higher water content resulted in improved anatase crystallinity.

Control of films' thickness of mesoporous titania using EISA has been also reported. Chen et al [Che-2008] have engineered very thick mesoporous TiO_2 crystalline films. In this case, a series of surfactant-templated mesoporous TiO_2 films with the

thickness over several micrometers have been successfully synthesized by one-step dip-coating. Three different pre-condensed TiO_2 sols in the presence of surfactant (Pluronic F127) micelles with high viscosities were employed as the precursors for dip-coating. By treating the films in liquid paraffin as a shape protector like at high temperature for sufficient time, thick mesoporous films can be kept crack-free after calcinations. By employing the size-controlled titanium-oxo clusters in the sols as building blocks for self-assembly, the final synthesized films exhibited tunable mesostructures. While the mesoscopic characteristics of the films, such as BET surface areas, pore size distributions and pore wall crystallizations, have been comparatively studied, the results demonstrated that such tunable mesoscopic characteristics are greatly dependent on the structural and shape parameters of the initial formed inorganic clusters.

Lastly, one should mention that the spatial ordering in the evaporation induced self assembly meso-porous TiO_2 can be enhanced by photo-induction [Rat-2007]. The method using a novel diblock KLE provides fully crystalline mesoporous layers of TiO_2 exhibiting high thermal stability up to 700°C , high photocatalytic activity in the decomposition of methyl stearate and facile transformation into a substantially stable super hydrophilic state by $1\text{mW}/\text{cm}^2$ UV-illumination.

4.1.2 Experimental observations of the induced ordering during the EISA of mesoporous TiO₂

Despite the numerous and diverse synthesized and studied nano-porous systems by evaporation induced self-assembly, only limited cases were investigated to shed light on to the growth process of the porous structure and its dynamic. The first deep insight in the mechanisms involved in the self-assembly of 2D-hexagonal templated mesostructured films during dip-coating in particular SiO₂ and TiO₂ based ones, Grosso et al and Gibaud et al have conducted grazing incidence small angle X-ray scattering (GISAXS) and X-ray reflectometry (XRR) investigations respectively to shed light the involved mechanisms [Gros-2004, Hen-2007]. The present part deals with the analysis of the mechanisms involved in the formation of TiO₂ highly organized 2D-hexagonal meso-structured films using Brij 58 as surfactant. The preparation of such films by dip-coating involves rapid evaporation which makes the different steps difficult to control. Simultaneous in-situ combined GISAX and interferometry analysis has been performed to obtain an initial understanding of the self-assembly process. In addition to TiO₂ mesoporous end materials, SiO₂ was also considered aiming to have a generalized view about the evaporation induced self assembly phenomena. TiO₂ and SiO₂ have different chemical reactivities in terms of kinetics and coordination aspects. However, as per discussed subsequently, Grosso et al [Gros-2004] showed that the mechanisms involved during dip-coating are quite similar. More precisely, the self-assembly leading to the organized phase takes place at a final stage of the drying process, involving the formation of a dis-organized intermediate phase and depending besides on the presence of micellar interfaces in addition to film/air and film/substrate interfaces. In the specific study of Grosso et al [Gros-2004], the growth dynamics of the 2-Dhexagonal TiO₂ mesoporous thin films, using TiCl₄ as precursor, Brij 58 as structuring agent in a water/alcohol medium (Molar ratios were: TiCl₄:1, Brij 58:0.58, EtOH: 40 and H₂O:10, relative humidity of

53%) were followed in-situ during the evaporation induced self assembly phenomenon. In this study, more emphasis was given to the comprehension of the self-assembly mechanisms taking place during the dip-coating and the evaporation process. The formation of any mesoporous material by evaporation induced self assembly process involve a rapid evaporation of the volatile molecules, which induces simultaneously the formation of the mesophase and the polycondensation of the inorganic entities giving rise to the final product. Hence, the study of the growth and ordering dynamics are complex processes. These later components are governed by the interactions existing at interfaces between organic and inorganic phases present in the system. Figure 25 represents the in-situ time resolved study of the TiO_2 based film formation during dip coating as revealed by simultaneous small angle x-ray scattering measurements. About 15 s after the starting of the evaporation induced self assembly process, the film is still drying as no diffraction is observed. The drying limit seems to be reached after 110s, which suggests that most of the liquid phase has departed the system after this point. The first diffraction signal is a low intense and homogeneous ring that starts to appear at about 135s and grows in intensity up to 7s after the drying line. This latter diffraction ring is characteristic of a worm-like structure whereby the organic micelles are elongated and randomly oriented within the film. From 190s, the ring is progressively replaced by diffraction spots and the whole transformation process lasts around 20s. The diffraction spot positions are unmistakably characteristic of a 2D-hexagonal structure with an average lattice parameter $\langle a \rangle$ of 6.6 nm. In this position, the micelles are hexagonally compacted and preferentially aligned with the surface of the substrate. The diffraction spot intensity increases in a continuous way for several minutes. The last observed phenomenon is the contraction of the normal to the surface deduced from the extension of the diffraction pattern in the corresponding direction.

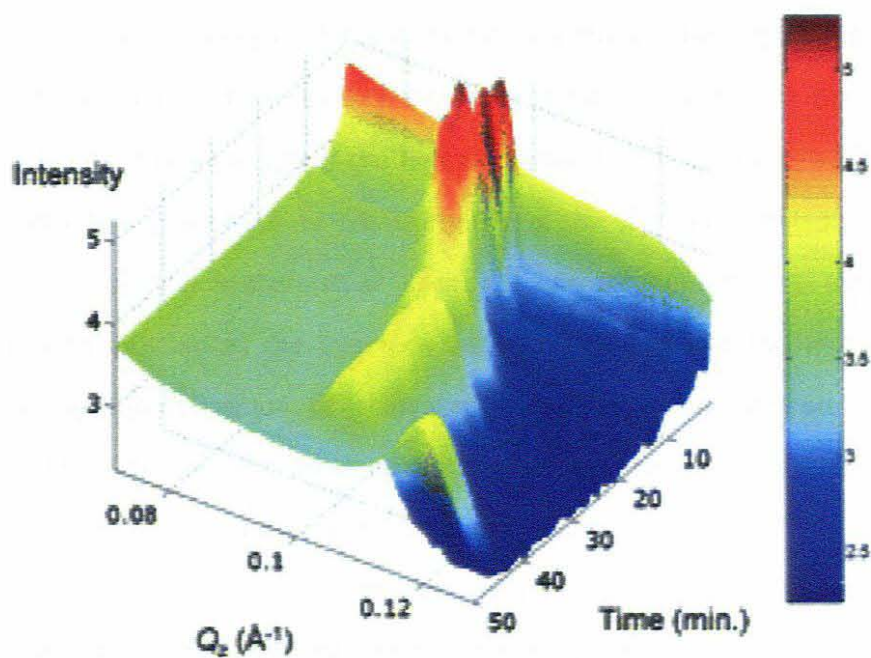


Figure 25: Representation of the in-situ time resolved study of the TiO₂ based film formation during dip coating as revealed by simultaneous small angle x-ray scattering measurements [Son-2008].

Grosso et al [Gro-2004] have proposed a model whereby the experimentally observed mechanisms involved in the formation of the meso-porous TiO_2 structure are summarized schematically as indicated in Figure 26. The initial stage corresponds to the evaporation of the liquid phase up to the drying line (Evaporation of EtOH and H_2O). During the second stage, the evaporation is lower and micelles start to form at the air/film interface in the first part. This results in the well observed worm-like structure which progresses toward the film/substrate interface as the concentration in surfactant molecules increases with time (from the bottom to the surface of the film). During the third stage, the film thickness seems to stabilize while the worm-like structure progressively transforms into the 2D-hexagonal structure. It was concluded by the authors that such a transformation is not only due to the interaction existing at the interface between micelles and the inorganic network, promoting the formation of elongated micelles, but in addition caused by the presence of air/film and film/substrate interface that favors the alignment of the micelles. Thus, the 2D-hexagonal structure of the mesoporous TiO_2 grows from the interfaces towards the film centre by re-organization alignment of micelles. Once the organized structure is formed, the film continues to dry and condense, inducing the observed uni-axial contraction of the structure generally observed in such films.

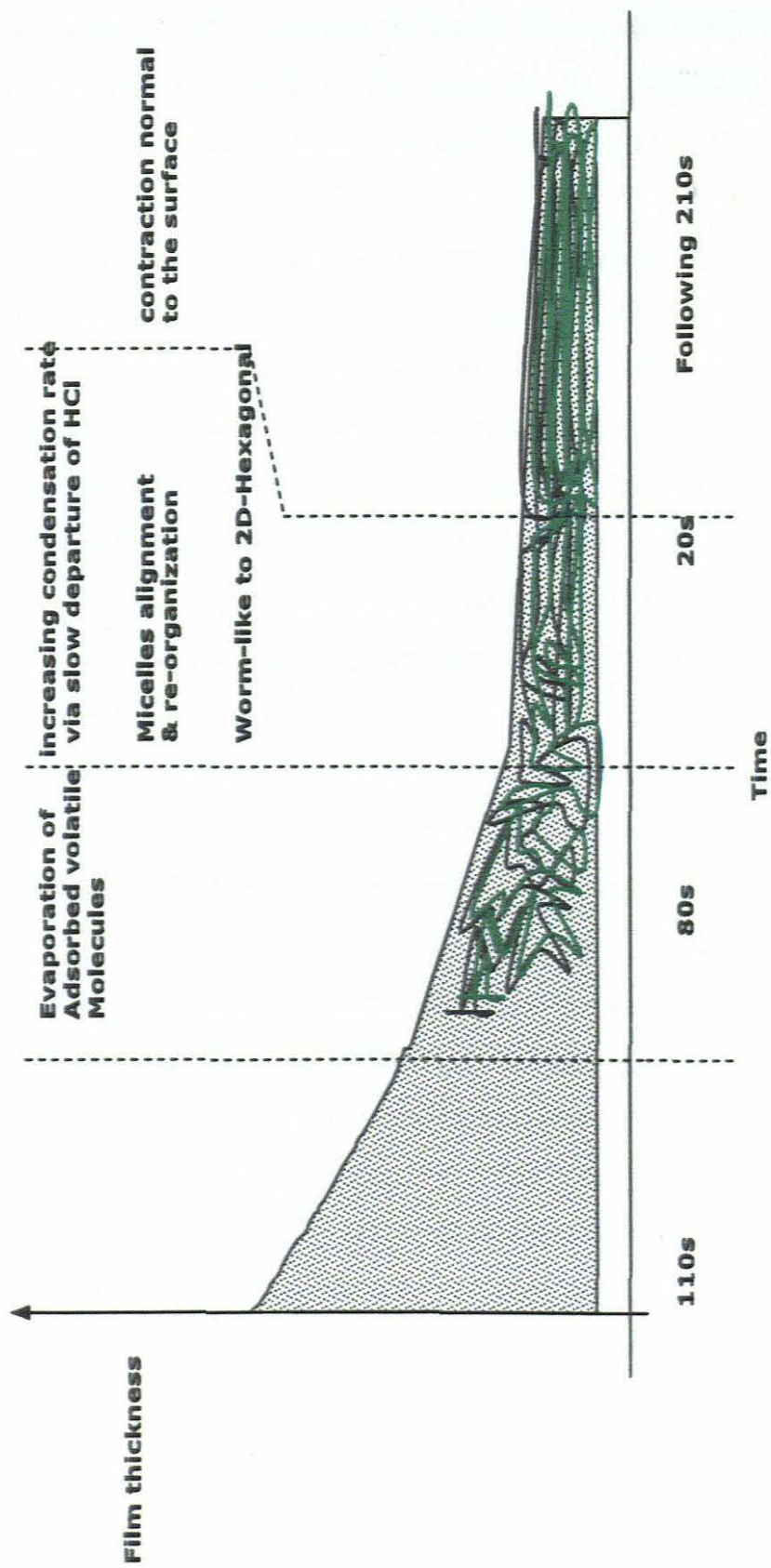


Figure 26: Formation 2-D hexagonal TiO_2 mesostructure.

Similarly to the small angle X-rays scattering work of Grosso et al [Gros-2004]. Recent experimental studies by Henderson et al and Gibaud et al have sustained the general observed trend in the case of TiO_2 [Hen-2004]. In this case, a complementary x-ray technique was used: XRR.

This latter technique was used to monitor the structural development of Titania based film at the solid-air interface using a nonionic poly (ethylene oxide) based surfactant and Brij 58 as the template and titanium chloride as the inorganic precursor. The reflectivity pattern, film thickness and refractive index were observed to be dependent on film deposition method, whether by casting or by dip-coating on silicon wafers as well as the Brij58/ TiO_2 ratio in addition to the humidity. More precisely, at Brij 58 content of 40%, the reflectivity profile displayed only a single diffraction peak. At 70% Bragg diffraction indicated a lamellar ordering of the film components. Modeled reflectivity data suggested a 106 nm thick film that comprised approximately 17 layers of alternating surfactant and Titania with a «d» spacing of the order of 6 nm. This latter experimental trend clearly indicates the re-organization and ordering of the nano- TiO_2 and the template host matrix.

This simulation approach to explain the observed experimental evolution of the small angle X-ray spectrometry by Grosso et al and the XRR by Henderson et al have been sustained by numerous theoretical modelings, among them one should mention the work of Hurd and Steinberg [Hur-2001]. Figure 27 shows the 2D diffraction patterns of various types of prepared mesostructures, together with corresponding TEM images and models depicting the preferential orientation of domains [Gro-2004]. To explain the degree of order in the resulting meso-porous ceramic phase which can be enhanced and controlled by continuous dip-coating in which the solution, initially dilute, evolves through the critical micelle concentration by steady-

state evaporation, a 3 steps model was suggested. The long range order and micro-structural orientation in these meso-porous films suggest that the propagation of a critical-micelle-concentration transition front, with large physico-chemical gradients, promotes oriented self assembly of surfactant aggregates. This so called "steep-gradient" view is supported by results from unsteady evaporation of aerosols of similar solutions, in which internally well ordered but complex particles are formed. The following section presents the most comprehensive fluid mechanics model which fits in general with the evaporation induced self assembly observations in general.

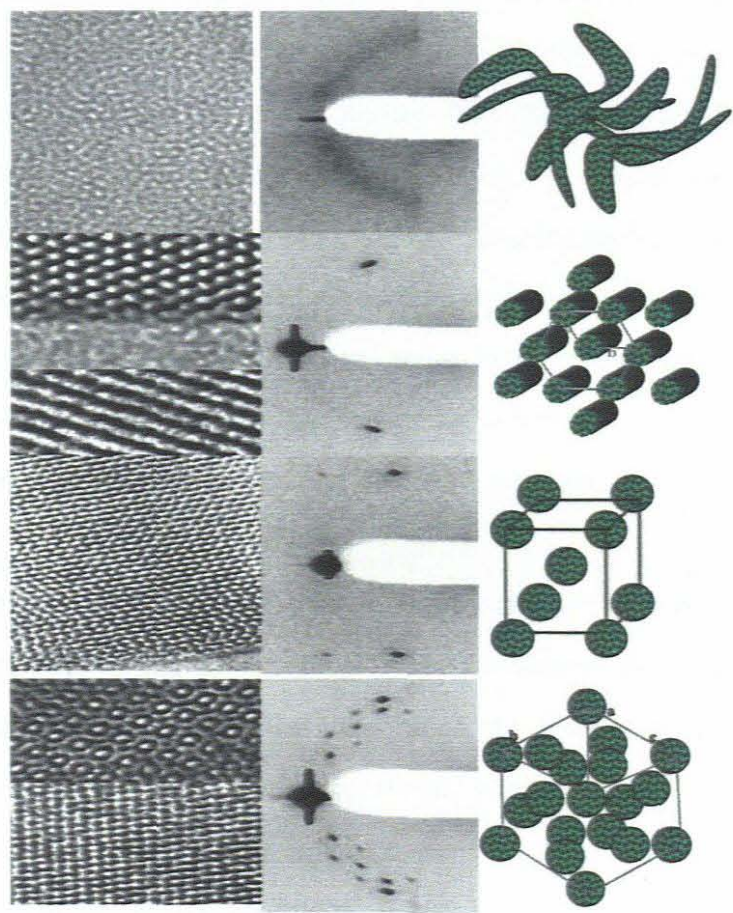


Figure 27: Typical 2-D diffraction patterns corresponding to various types of mesostructures together with corresponding TEM images [Gro-2004].

4.1.3 Modeling of the rheology change during the EISA process

The observations by Grosso et al [Gro-2004] were confronted to additional theoretical models by Madras and McCoy [Mad-2006]. In this model, it is shown that the self-assembly from a metastable state often occurs by nucleation accompanied by nano-particles growth and ultimately by Ostwald coarsening. By developing a population balance model for growth and coarsening, Madras et al [Mad-2006] model allows the determination of the dynamics of the self-assembled cluster size distributions in 2 or 3 dimensions. While the governing equations were solved numerically, the asymptotic coarsening stage revealed a power-law increase in the average particle mass as the cluster size distribution evolves to a minimum of polydispersity index of unity for both 2-D and 3-D phases transitions. In addition, by incorporating the solvent evaporation to simulate drying mediated self-assembly of the nano-particles, the model produced a temporal law relationship with an exponent of $\frac{1}{4}$ for the average 2-D domain radius, in agreement with experimental observed behavior. Likewise, it was found that the power law relationships can be found by varying the coalescence rate and the power on mass as well.

Additionally to the previous models, Newtonian and hydrodynamics approaches were investigated. As the self assembly of nano-structures during the evaporation induced self assembly is driven by the evaporation of the sol, it is required to understand the influence on the hydrodynamics of the solution. So far, the published work on evaporation related hydrodynamics problems has mainly focused on Newtonian fluids. Qu et al [D Qu-2002] examined experimentally and theoretically the hydrodynamics of evaporative poly-dimethylsiloxane during dip-coating and observed that the film thickness follows a similar power law as nonevaporative fluid films. Das Gupta et al [Das-1993] investigated an evaporating meniscus using the

Young-Laplace equation while Wayner [Way-1993] examined the spreading/wetting of a liquid film with a finite contact angle by the evaporation/condensation phenomenon and demonstrated that the evaporation/condensation process may have a consequential effect on the contact line movement. Moosman et al [Moo-1980] modeled the transport processes occurring in an evaporating meniscus using a perturbation theory approach. It has showed that non negligible heat flux may occur in the transition region between the capillary meniscus and the adsorbed layer [Fre-2005] studied the close wall dynamics and thermodynamics of evaporating menisci using atomistic simulations of a Lennard-Jones type fluid. Heurd et al [Heu-2001] used the so called «the steep-gradient» concept. It was then suggested that the long range order and micro-structural orientation in the then formed nano-structured films is closely related to the propagation of a critical micelle-concentration transition front. In addition to the fluid based approaches, Monte Carlo [Rot-2000, Ran-2000] as well as density functional [Fri-1999] simulations have been used to shed light on the self assembly process.

Besides, the above mentioned theoretical models, one should mention the theoretical approach used by Lee et al [Lee-2008]. This latter contribution seems to be the most complete so far in explaining the self-assembly process based on a fluid flow model via a complete study of the rheological properties of the self assembled film. More accurately, the film formation model was based on the lubrication approximation with evaporation effect. It is shown that evaporation induced self-assembly leads to rheological variations in the entrained film and consequently, alters the film thickness and the spatial ordering. As this rheology based model fits superbly with the experiments, it is presented in detail within this theoretical section. In this model, the coating is considered as a thin layer applied dynamically to a solid substrate S.F. Kistler et al, in Liquid film coating-Scientific principles and their

technological implications [Scr-1962, Rus-1985, Dor-1997] and the focus is on the evaporation effect during the fluid coating in a non Newtonian approach [Bre-1961]. In Lee et al's model, the primary focus was to consider the evaporation induced rheology change in the entrained film and develop an evolution equation of the film thickness $h(x, t)$ based on fundamental fluid flow and contact angle parameters and to predict the steady state of the film thickness and meniscus shape. In such a configuration schematized by Figure 28 where the flat substrate moves with a constant velocity U with a predicted constant steady state film thickness h_0 , the governing equations are deduced from nonlinear differential equations as follows:

$$\text{div } \mathbf{u} = 0$$

$$\rho \, d\mathbf{u}/dt = -\text{grad } p + 2 \, \text{div } (\eta \, \mathbf{D})$$

$$\rho \, c_p \, dT/dt = -\text{div } (\lambda \, \text{grad } T)$$

where $\mathbf{v} = (u, v)$, q and p are the velocity, absolute temperature and pressure. ρ , η and c_p and λ are the density, shear viscosity, specific heat, and thermal conductivity of the sol. $\mathbf{D}$ is the strain-rate tensor defined in terms of the velocity gradient $\mathbf{L} = \text{grad } \mathbf{u}$ by $\mathbf{D} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^T)$. For low dip-coating velocities, η remains constant with varying shear rates. λ and c_p are considered as constants. Generally η is expected to vary with concentration. In the lubrication approximation, this effect should result in a dependence of η on the film thickness. In this model, η is considered empirically as function of the film thickness.

The mass balance requires that the net mass flux normal to the film surface obeys to:

$$j = \rho (\mathbf{u} - \mathbf{u}_s) \cdot \mathbf{n} = \rho_v (\mathbf{u}_v - \mathbf{u}_s) \cdot \mathbf{n}$$

With ρ_v and $\mathbf{u}_v$ the mass density and the velocity of the vapour while $\mathbf{u}_s$ and $\mathbf{n}$ are the velocity of the surface and the unit orientation of the interface (directed into the vapour). Introducing $\mathbf{u}_s \cdot \mathbf{n} = h_t / \sqrt{(1+h_x^2)}$, one could rewrite j expression as:

$$J = \rho (v(h) - u(h) h_x - h_t) / \sqrt{(1+h_x^2)}$$

The momentum balance on the film surface requires that the following equation must be fulfilled:

$$\sigma K \mathbf{n} + \text{grad}_s \sigma = 2 \eta \mathbf{D} \cdot \mathbf{n} - (p - p_v + \Pi - j^2/\rho_v) \cdot \mathbf{n}$$

Where s is the equilibrium surface tension of the sol-gel solution with the initial concentration before the evaporation occurs, K is the curvature of the film surface, p_v is the vapour pressure and grad_s is the gradient of the film surface, and Π is the disjoining pressure. This disjoining pressure can become significant if the film thickness is less or equal approximately to 20nm as demonstrated by Davis [Bur-1988]. It has the following form for a completely wetting system:

$$\Pi = A / (6 \pi h^3)$$

where A is the so called Hamaker constant, $A > 0$. It assumes values of about 10^{-19} . If the film thickness is small, van der Waals effect can become significant. After scaling analysis, it could be observed that can be neglected when compared to other terms. Hence the energy balance requires that:

$$(\lambda \text{ grad} T) \cdot \mathbf{n} = -L j$$

with L is the latent heat of vaporization. In addition one should consider the kinetics of evaporation/condensation by imposing the Hertz-Knudsen relation:

$$j = j_T (T_s - T_v)$$

with T_s and T_v , the film surface and the vapour temperatures respectively and is a physical parameter depending on the saturation temperature and molecular weight of the solvent. A standard value for j_T is about $3.56 \text{ kg/s m}^2\text{K}$. At last, one should consider the boundary conditions on the substrate which are simply:

$$u = -U$$

$$v = 0$$

$$T = T_0$$

where U is the constant coating speed and T_0 is the constant temperature at the sol reservoir. To deduce the relative film thickness variation h' in a concise way, Lee *et al* have used dimensionless parameters. If one introduces the characteristic length scales in the x and y directions, the length-scale in the x direction that is parallel to the substrate is an unknown value l_∞ . This corresponds to the length scale over which the free surface curvature variations are important. The length scale in the y direction is the film thickness h_0 far away from the sol reservoir. The lubrication limit was considered where $\varepsilon = h_0 / l_\infty \ll 1$ and $v \ll u$. The dimensionless variables were defined as: $h' = h/h_0$, $x' = x / l_\infty$, $u' = u / U$, $v' = v / U$, $j' = j/j_0$, $\eta' = \eta/\eta_0$, $\sigma' = \sigma/\sigma_0$, $T' = T/T_0$ and $p' = p/P$. j_0 is the characteristic evaporation rate of the bulk sol-gel solution that can be measured experimental. D_s is defined as the maximum surface tension variation along the meniscus and P is defined as $P = \eta_0 U l_\infty / h_0^2$, P is then the reference pressure when viscous force balances capillary pressure from the momentum balance. If one strict the treatment to a steady state coating with the

standard assumption of $h_x \ll 1$, $h_t = 0$. Thus at the film surface $y' = h'$, the dimensionless boundary conditions are:

$$p' = -\sigma_0 h_0 \sigma' h_x / (P l_\infty^2) + j_0^2 j'^2 / (P \rho_v) - A / (6 P h_0^3 \pi h'^3)$$

$$\sigma_x' = \eta_0 U l_\infty^2 \eta' u_y' / (\Delta \sigma_0 h_0)$$

$$T y' = -L j_0 h_0 j' / (\lambda T_0)$$

$$j' = j T_0 (T_s' - T_v') / j_0$$

Moreover, at the substrate the dimensionless boundary conditions are:

$$u' = -1$$

$$v' = 0$$

$$T' = 1$$

If one introduces the following dimensionless numbers

$C = \eta_0 U / \sigma_0$	Capillary number
$C^* = \epsilon^3 / C$	Effective capillary number
$A^* = A / (6\pi \eta_0 U h_0 l_\infty)$	Van der Waals number
$V^* = j_0^2 h_0^2 / (\rho_v \eta_0 U l_\infty)$	Vapor recoil number
$G^* = \rho g h_0^2 / (\eta_0 U)$	Gravity number
$M^* = \epsilon \Delta \sigma / (\eta_0 U)$	Marangoni number
$E^* = j_0 / (\epsilon \rho U)$	Evaporation number

Hence one obtains the dimensionless film thickness h' within a nonlinear form as:

$$[-h' + C^* h^3 \sigma' h'_x / 3\eta' + A^* h'^3 / (3\eta' h_x^3) - V^* h'^3 j_x^2 / (3\eta') - G^* h'^3 / (3\eta') + M^* h'^2 \sigma_x / (2\eta')] + E^* j' = 0$$

The dimensionless numbers in the equation exhibit the balance among viscous stresses, capillary pressure, intermolecular forces, Marangoni forces, gravity and evaporation effects. For a typical Evaporation Induced Self Assembly-sol gel type solution, the values are of the order of : $j_0 \sim 0.26 \text{ mg/s cm}^2$, $\eta_0 \sim 2,23 \text{ mPa.s}$, $\sigma_0 \sim 22.4 \text{ mN/m}$, $\rho \sim 867 \text{ kg/m}^3$, $\rho_v \sim 0.6 \text{ kg/m}^3$, $U \sim 100 \text{ mm/min}$. Therefore, it is possible to estimate the capillary number C which is about $1.66 \cdot 10^{-4}$ i.e. $C^* \sim 1$. The other dimensionless numbers are of the order of $V^* \sim 7.2 \cdot 10^{-8}$, $A^* \sim 1.2 \cdot 10^{-4}$, $G^* \sim 2.1 \cdot 10^{-4}$ and $E^* \sim 0.02$. Hence with the capillary ($C^* \sim 1$) and evaporation effects ($E^* \sim 0.02$) are dominant compared to the other factors such as vapour recoil effect ($V^* \sim 10^{-7}$), van der Waals effect ($A^* \sim 10^{-4}$) and gravity effects ($G^* \sim 10^{-4}$) but still with a very important contribution from Marangoni component.

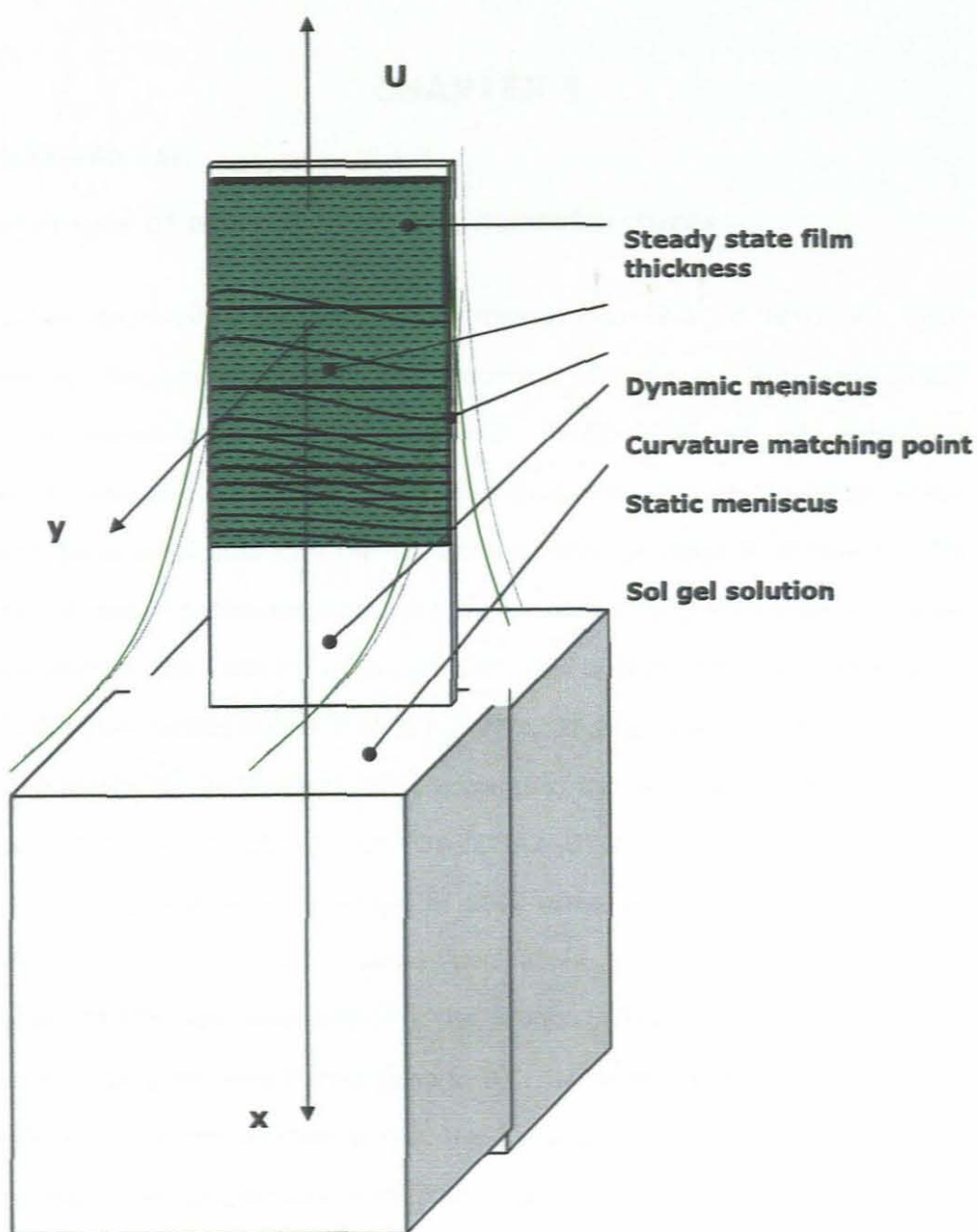


Figure 28: Schematic representation where the flat substrate moves with a constant velocity U with a predicted constant steady state film thickness h_0 .

CHAPTER 5

5. EXPERIMENTAL

5.1 Synthesis of mesoporous TiO₂ nanostructures

As mentioned previously, the investigated mesoporous films of nano-TiO₂ were synthesized by Evaporation Induced Self Assembly «EISAA» at room temperature following the procedure invented by Alberius *et al* [Alb-2002] but with some few modifications. Mesoporous nano-TiO₂ were deposited onto Indium Tin Oxide «ITO» coated float glass substrates with the square resistance of about 8 8Ω/square. The conducting ITO coated substrates and all the chemicals that were used were purchased from Sigma-Aldrich. The following chemicals were used as precursors: HCl "37%, 6,4g, 63mmol", Titanium isopropoxide "Ti (OⁱPr)₄, 97%, 10.24g, 35mmol", Pluronic P123 triblock co-polymer "2g, 0.34mmol". More accurately, the used Pluronic P123 triblock co-polymer, HO"CH₂CH₂O"₂₀[CH₂CH"CH₃"O]₇₀"CH₂CH₂O"₂₀H, simply represented as "EO"₂₃-"PO"₇₀-"EO"₂₃ with a molar weight of 5800 g/mol was dissolved in ethanol of 98% purity. The P123-Ethanol solution was about 24g/5.18mmol. Firstly, the concentrated HCl 37% was slowly added to the solution of Titanium isopropoxide under vigorous stirring at a low temperature close to 0°C. The main reason in conducting the synthesis at such low temperature is that the formation of the P123 cubic phase is facilitated below room temperature [Alb-2002]. Afterwards, the clear colorless solution of P123 was first dissolved in Ethanol separately and then added into the HCl/ Titanium isopropoxide solution. This obtained clear yellow solution was subsequently aged with stirring at room temperature for 22hrs.

The mesoporous TiO₂ films were then prepared by dipping the conducting ITO coated float glass substrates into the fresh diluted solution at a rate of 2.4 cm min⁻¹ using a custom built dip- coater equipped with a humidity chamber at the University of Le

Mans. After each dip-coating phase, the ITO coated substrates were withdrawn at the same rate right after an immersion time of 1min. The relative humidity "RH" was increased to 40% RH and maintained for a period of about 2-3 minutes. Thereafter, the dip coated ITO-glass samples were removed from the chamber and allowed to remain in ambient conditions for ~10munites while sealed in a glass Schott bottle in air and stored within a temperature range of 5-10°C for 24-48 hrs prior to analysis. The samples were then calcined at ~600°C for 4 hrs hours to remove the block copolymer species and the surfactant and also to ensure the crystallization of the amorphous Titania to a crystalline form. Likewise, the calcined samples were subjected to an Ultraviolet «UV»treatment as this radiative treatment leads to highly ordered arrays of titania onto the conductive substrate. The 4 considered samples are labeled as TiO₂-A, TiO₂-ADIL, TiO₂-B and TiO₂-BDIL.

5.2 Results and discussion

5.2.1 Structural ordering and surface morphology

The SEM and AFM are known to be perfect tools for providing information about the surface morphology of the film, respectively. In this work, both of these tools were used to study the surface morphology of the films. The SEM images presented here were recorded from a High resolution Scanning Electron Microscopy operated at 20kV to observe the surface morphology of TiO_2 mesoporous nanoparticles before and after calcination. The removal of polymer matrix by calcining the films at 600°C transformed the amorphous titania into crystalline titania which in general is the anatase phase. UV treatment on the other hand was used alternatively to also remove the polymer matrix. Figure 29 (a, b) shows the SEM images of the mesoporous TiO_2 films after calcination. The brighter colour observed from these images is associated with the presence of Titania nanoparticles. Titania films with higher Titania precursor seemed to behave completely different from those with small amount of Titania precursor in a sense that films with low amount of TiO_2 precursor showed irregular particles which are more randomly dispersed in the polymer matrix, as presented on figure 29 (a) and (b). As the precursor concentration was increased to 10 mol%, the uniform particles were observed although they tend to order in a hexagonal packing as indicated in figure 29(a, and b). It was also realized that after calcining at 600°C irregular worm like structures oriented perpendicular to the substrate were formed which might be due to the presence of unwanted impurities remained during calcination. However, after UV treatment the preserved long-range highly ordered mesoporous TiO_2 nano-rods with an average diameter of 20-30 nm and 350nm long were observed. These results strongly suggests that the moment a precursor is added, the originally ordered PEO domain arrangement in pure PEO-PPO-PEO is destroyed and also, the individual structure of titania nanoparticles is preserved after calcination or UV treatment.

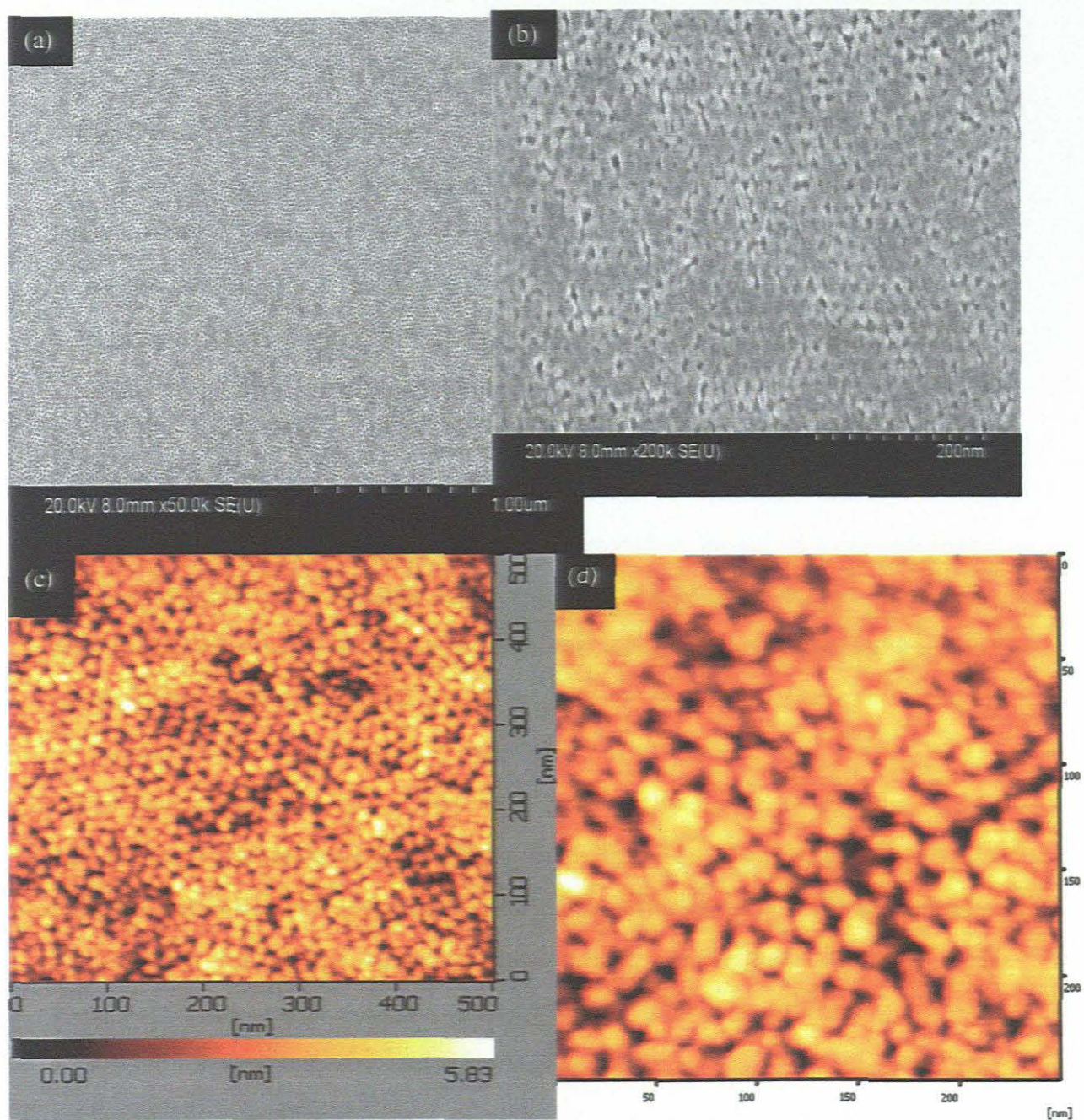


Figure 29: SEM (a, b) and AFM (c, d) images of the mesoporous TiO_2 films after calcination

The orientation of these films was supported by high resolution top view AFM images shown on figure 29 (c, d). These AFM measurements were carried out on an AFM Dimension 3000 with a Nanoscope IIIa controller. The images were obtained in an intermittent tapping mode using a Nanoscope IIIa controller with Multi Mode AFM head. The observed AFM images indicated mesoporous TiO₂ nanoparticles grown on the substrate and the low roughness of these films confirms the good homogeneity as well as good dispersion of TiO₂ nanoparticles. The obtained average particle size of TiO₂ mesostructures ranges between 30-41nm.

Beside the scanning electron microscopy (SEM) and the atomic force microscopy (AFM), the mesoporous TiO₂ nanostructures were investigated by means of X-ray reflectivity and grazing incidence small angle x-ray scattering. The usage of these techniques is essential to follow the order and disorder in the formation of the mesoporous nanostructured TiO₂ and thus to track the evolution of the films structure before and after calcinations. The X-ray Reflectometry (XRR) experiments were carried out using a θ -2 θ Phillips reflectometer with a CuK α radiation (1.545 Å) at the University of Le Mans [Son-2007]. The grazing incidence small angle X-rays scattering (GISAX) were performed on the ID01 instrument at the European Synchrotron Radiation Facility-Grenoble using a wavelength of 1.127Å. The exposure time was about 10s per frame and the incident angle was slightly greater than the critical angle of the substrate to allow penetration of X-rays into the film. Both X-ray Reflectometry and grazing incidence X-rays small angle scattering were performed within the framework of a joint French-South African cooperation program. Figure 30 displays typical room temperature X-ray reflectivity profiles before and after calcination reporting the relative reflected X-ray intensity (Reflected intensity/ incident intensity i.e. Reflectivity) versus the transversal momentum $Q_z = 2\pi \sin\theta/\lambda$ where θ and λ are the X-rays angle of incidence and their wavelength respectively. As it can be observed, the presence of Bragg diffraction peaks

before and after the calcinations at such a low incidence angle indicates a highly organized mesoporous structure. The calcined samples exhibit 2 narrow Bragg peaks while the non calcined samples exhibit only 1 wide Bragg peak. This points out that yet before and after calcinations, the mesoporous TiO_2 samples are organized phases, the calcined samples are much ordered (long range order). As the Bragg peaks' position is related to spatial ordering which is (110) d-spacing in this case, it is possible to deduce it before and after calcinations as $Q_{\text{ZBragg}} = 2\pi/d_{110}$. From Figure 29, the values of d_{110} are 9.8 nm and 6.6 nm before and after the calcinations respectively. This diminution of the d-spacing related to the ordering in the samples implies a significant shrinkage of the mesoporous TiO_2 and therefore their densification. More accurately, the reduction of the d_{110} spacing, one could deduce the contraction of the lattice parameter «a» as «a» = $d_{110} \sqrt{2}$. Hence the calcinations process of the mesoporous TiO_2 samples generates a substantial contraction of «a» from 13.9 nm to 9.3 nm i.e a relative variation of about $\Delta\text{«a»}/\text{«a»} \approx 33.1\%$. To concur this shrinkage of the synthesized mesoporous TiO_2 samples with the crystallographic modification following the calcinations treatment, grazing incidence small angle X-rays scattering investigations were carried out at room temperature. Figure 30 represents a typical corresponding 2-D profile. Subsequent to the calcinations treatment, the pattern reveals the presence of the body-centered cubic $Im3m$ structure with a lattice parameter of about «a» = 9.1 nm i.e. d_{110} of 6.3 nm. These values are in a good agreement with the values obtained by XRR. In fact, as per identified by Crepaldi et al [Cre-2003] and [Sol-2003], following the calcinations, the d_{110} distance of the $Im3m$ cubic phase is distorted by uniaxial shrinkage in the z-direction (direction perpendicular to the substrate). Hence, the contraction of the real structure is no longer $Im3m$ cubic but rather a face centered orthorhombic phase.

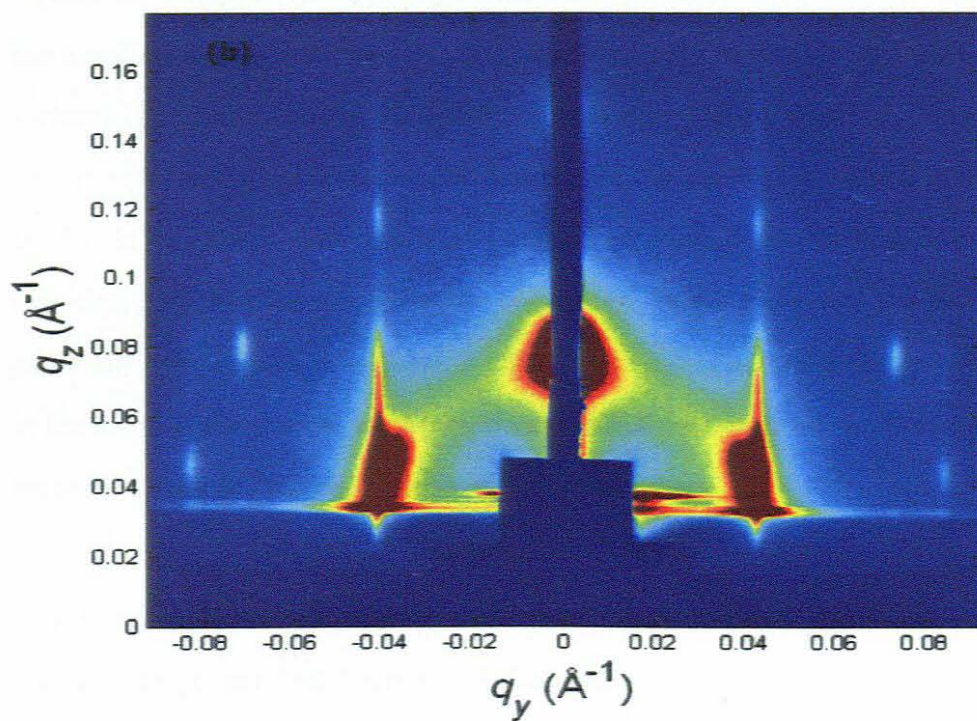
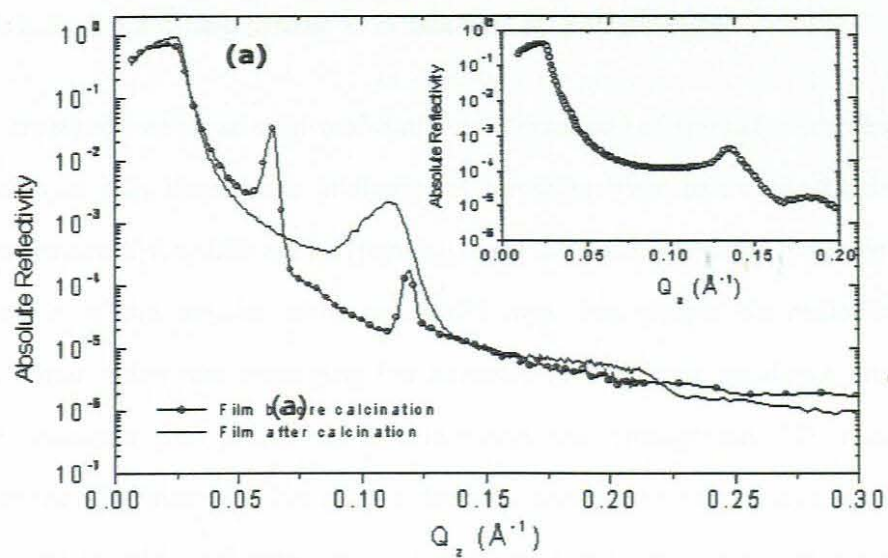


Figure 30: (a) Typical grazing incidence small angle X-ray scattering (GI-SAS) and (b) X-ray reflectivity profile of the investigated meso-porous TiO_2 films.

5.2.2 Crystallography and texturing properties

The crystallographic structure and phase information of the calcined mesoporous nano-structured TiO_2 films were analyzed by samples have been investigated using room temperature X-Ray Diffraction (Rigaku-denki 2200) in a grazing mode with the detector scanning in the angular range of 15-75 deg. The copper $K\alpha$ radiation of 1.5405 Å collimated beam was impinging the samples at a grazing incidence angle of 1.5 deg. This geometry was chosen so to probe only the mesoporous TiO_2 nanostructure and avoid the ITO layer and the glass substrate. Indeed, when one working with thin films, it is useful and preferable to use grazing angle geometries in order to limit the penetration of the X-rays and enhance the diffraction pattern of the thin film with respect to the substrate. Grazing Incidence is a scattering geometry which combines the Bragg condition with the conditions for X-Ray total external reflection from crystal surfaces. In Grazing incidence Diffraction, the penetration depth of X-Rays inside the slab is reduced by three orders of magnitude, typically from 1-10 μ to 1-10nm "10-100Å". In addition, below the critical angle typically between $\frac{1}{4}$ and $\frac{1}{2}$, the totally externally reflected wave penetrates only a few nanometers into the material, giving externally high surface sensitivity. A strong diffracted beam can be observed emerging at the same grazing angle as the incident beam if the specimen is located to satisfy the angle for Bragg Diffraction in plane of the sample.

Figure 31 reports the room temperature XRD patterns of the 4 different samples. As it can be noticed, the XRD patterns of the different samples are identical in trend. The diffraction patterns consist of 7 wide Bragg peaks located approximately at 25.28, 36.94, 38.57, 53.89, 55.06, 62.12 and 62.69 deg respectively (see Table 4). All these diffraction lines are quite similar to those of a bulk anatase with the exception of their weak intensities and large linewidths except the absence of the (112) peak. Hence, one

can deduce that the calcined mesoporous samples consist of quasi pure TiO_2 and that the TiO_2 crystallites possess a certain degree of long-range order of the anatase phase since the XRD usually reveals average structural information of several unit cells. However, the relatively weak intensity of the diffraction Bragg lines implies the presence of imperfect lattice sites. As the most intense Bragg peak is the (101), all the 4 mesoporous TiO_2 samples are textured along the (101) reticular direction. One could observe that there is a shoulder peak localized at about 24.8 deg.[°] This peak is persistent in all the 4 samples. This could be attributed to the (120) brookite TiO_2 nano-crystals.

As pointed out, the Bragg peaks are significantly wide with an average angular width of about $\beta \sim 0.6$ deg implying the nano-scaled size of the TiO_2 crystallites. The Scherer's equation which is given by $D = k\lambda / \beta \cos \theta$ (where k is a constant "shape factor, about 0.9), allows the estimation of the average size of the TiO_2 nano-crystallites. As reported in Table 4, the average size is within the range of 12 and 15 nm. If one considers the major Bragg peak i.e. (101), one can notice that the TiO_2 nano-crystallites' size is approximately identical if one considers the bar error for both TiO_2 -14B and TiO_2 -14A series; it is about 14.5 nm. This indicates that the considered surfactant concentration range and the film thicknesses do not influence the size of the then formed TiO_2 crystallites in the mesoporous form.

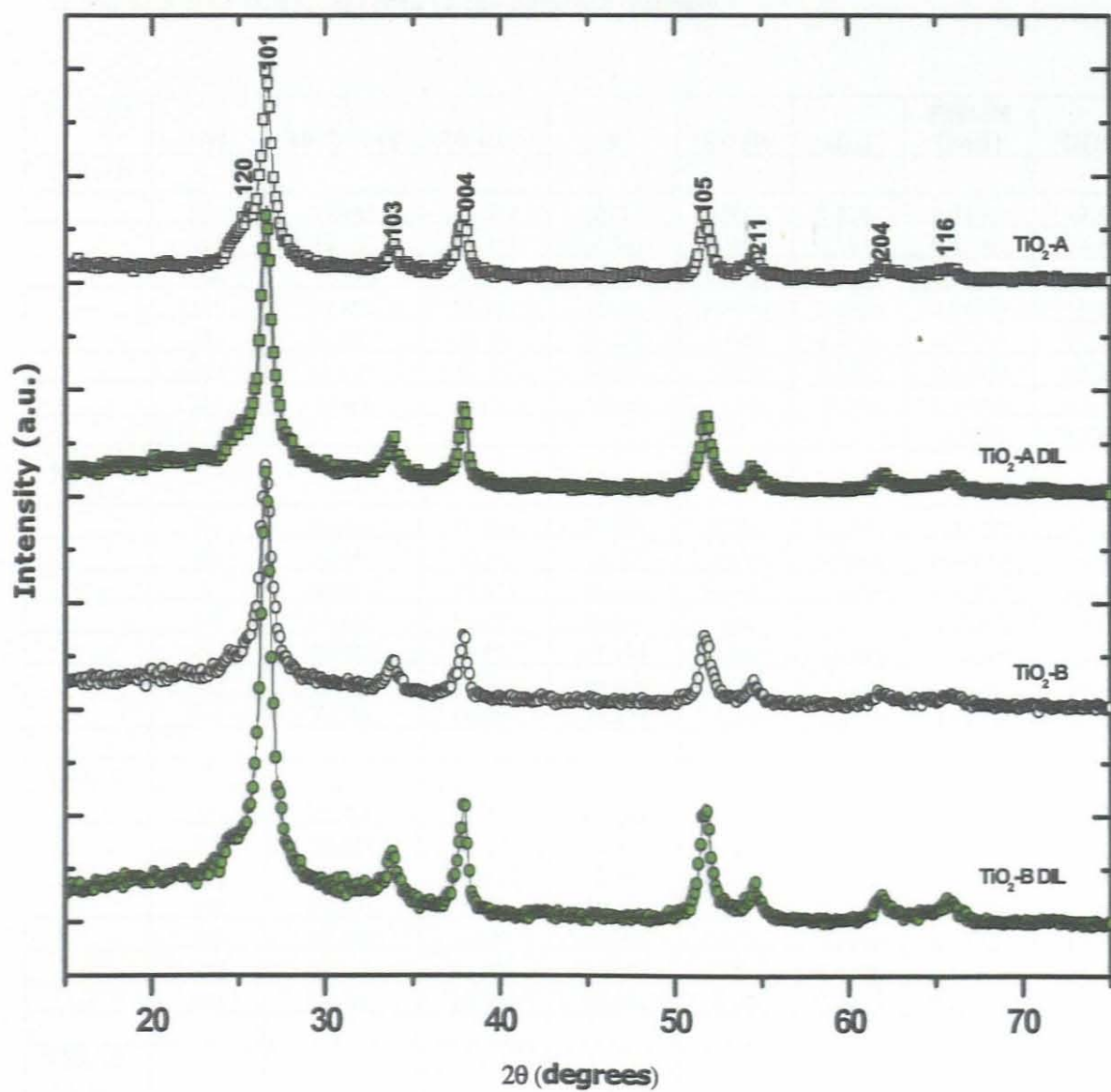


Figure 31: Room temperature grazing incidence XRD patterns of different mesoporous nano-structured TiO_2 films after calcination.

Table 4: X-Ray Diffraction data of the different samples.

Sample	hkl	2 θ theory	2 θ exp.	θ	Cos θ	d _{hkl}	FWHM (rad)	D(nm)
TiO₂-A								
	101	25.281	26.582	13.291	0.973	0.3351	0.01097	12.9758
	103	36.947	33.911	16.956	0.957	0.2641	0.01005	14.4067
	004	38.576	37.911	18.956	0.9458	0.2371	0.00986	14.8611
	105	53.891	51.794	25.897	0.8999	0.1763	0.01007	15.2943
	211	55.062	54.51	27.255	0.889	0.1682	0.01221	12.7614
	213	62.121	61.99	30.995	0.857	0.1495	0.00938	17.2241
	204	62.69	65.7	32.85	0.84	0.142	0.01713	9.62738
							AVERG	13.8787
TiO₂-A DIL								
	101	25.281	26.558	13.279	0.973	0.3352	0.01197	11.8977
	103	36.947	33.86	16.93	0.957	0.2644	0.01032	14.0268
	4	38.576	37.931	18.966	0.9458	0.2369	0.00876	16.7261
	105	53.891	51.778	25.889	0.8999	0.1764	0.01019	15.1109
	211	55.062	54.497	27.249	0.889	0.1682	0.01288	12.1043
	213	62.121	61.932	30.966	0.857	0.1497	0.01286	12.5733
	204	62.69	65.754	32.877	0.84	0.1419	0.01689	9.76661
							AVERG	13.1723
TiO₂-B								
	101	25.281	26.558	13.279	0.973	0.3352	0.01092	13.038
	103	36.947	33.93	16.965	0.957	0.264	0.01570	9.22028
	4	38.576	37.901	18.951	0.9458	0.2371	0.01221	11.995
	105	53.891	51.76	25.88	0.8999	0.1764	0.01570	9.80532
	211	55.062	54.49	27.245	0.889	0.1682	0.01221	12.7614
	213	62.121	61.811	30.906	0.857	0.1499	0.01221	13.2379
	204	62.69	65.769	32.885	0.84	0.1418	0.01396	11.8176
							AVERG	11.6965
TiO₂-B DIL								
	101	25.281	26.562	13.281	0.973	0.3352	0.01047	13.603
	103	36.947	33.78	16.89	0.957	0.2651	0.00872	16.5965
	4	38.576	38	19	0.9458	0.2366	0.01047	13.9942
	105	53.891	51.7	25.85	0.8999	0.1766	0.00872	17.6496
	211	55.062	54.548	27.274	0.889	0.168	0.01047	14.8883
	213	62.121	61.8	30.9	0.857	0.15	0.01221	13.2379
	204	62.69	65.7	32.85	0.84	0.142	0.01570	10.5045
							AVERG	12.9758

5.2.3 Optical and band-gap properties

The room temperature transmittance and diffuse reflectance were recorded on a UV-VIS-NIR spectrophotometer (Shimadzu UV-3150) in the range of 250-1800 nm. Figure 32 (a) shows the typical optical transmittance profile at normal incidence of the different mesoporous nano-structures TiO_2 films. It can be noticed from this transmittance spectra that the films deposited onto the FTO coated glass substrates are optically transparent in the investigated spectral range; T is in the scale of 70-85% which within an average of the order of 75%. The optical transmittance profiles exhibit optical interference fringes patterns which are related to their limited film thicknesses. The standard minima-maxima envelope of the optical transmission have been used to deduce both the mesoporous films thicknesses $\langle d \rangle$ and their average refractive index $\langle n_{\text{Film}} \rangle$. The Napierian absorption coefficient of each sample can be calculated using the Lambert's law,

$$\alpha \sim 2.303 (-\log (T)/\langle d \rangle)$$

$\langle d \rangle$ can be determined using the relation:

$$\langle d \rangle = \lambda_1 \lambda_2 / 2 [\lambda_2 n(\lambda_1) - \lambda_1 n(\lambda_2)]$$

where λ_1 and λ_2 are the wavelengths corresponding to two adjacent maxima or minima and $n(\lambda_1)$ and $n(\lambda_2)$ at λ_1 and λ_2 , respectively. The refractive indices of the titania mesoporous films were calculated using the transmittance spectrum in the range of 240-1800 nm employing Manifacier's method [Man-1976]

$$n(\lambda) = \sqrt{[S + \sqrt{S^2 - n_0^2(\lambda) n_s^2(\lambda)}]}$$

$$S = \frac{1}{2} [n_0^2(\lambda) + n_s^2(\lambda)] + 2n_0(\lambda) n_s(\lambda) [(T_{\max}(\lambda) - T_{\min}(\lambda)) / (T_{\max}(\lambda) T_{\min}(\lambda))]$$

Where $n_0(\lambda)$ and $n_s(\lambda)$ are the refractive indices of air and the film respectively. $T_{\max}(\lambda)$ and $T_{\min}(\lambda)$ are the maximum and the minimum envelopes respectively. From the transmission spectrum, the refractive index of the substrate which consists of the thick FTO coated glass substrate is calculated as a function of the wavelength using:

$$n_s(\lambda) = 1/(T_s(\lambda)) + \sqrt{[(1/T_s^2(\lambda)) - 1]}$$

where T_s is the transmittance of the substrate. Table 5 reports the different deduced optical data for all samples except sample TiO₂-A as there are only few minimas/maximas in which case the Manifacier's envelope method could not be applied with a high precision. As one can see, the average value of the refractive index of the mesoporous TiO₂ films is about 1.5 which is far smaller relatively to bulk anatase value which is about 2.56. This is due to the high porosity of the investigated meso-porous TiO₂ films as sustained by Figure 32 (b) reporting the diffuse reflectance of the different samples. As per shown in Figure 32 (b) reporting the diffuse reflectance variation, it is noteworthy to observe that the reflectance values are lower than that of bulk polycrystalline TiO₂. TiO₂ has a high refractive index which is about $n_o = 2.56$ (ordinary refractive index) and $n_e = 2.49$ (extra-ordinary refractive index) for anatase. Therefore, it is difficult to obtain a low reflective thin film coating of single component of TiO₂. Hence, the low optical reflectance and large transmission are correlated to the regular porosity of the meso-porous films. By using Yoldas-Partlow's model [Yol-1985], it is possible to estimate the nanostructures' porosity. This later is given by:

$$\text{Porosity} \sim 100 [1 - (n^2 - 1) / (n_{\text{bulk}}^2 - 1)]$$

As per mentioned above, the refractive index of the bulk dense TiO₂ anatase is about 2.5, therefore the average porosity of the meso-porous TiO₂ films is about 76%, indicating their very high porous architecture. This is not surprising if one considers the optical transparency of the samples in terms of their high optical transmission. In addition, the very low diffuse reflectance exhibited by all samples even if reinforced by interference for some wavelengths. This indicates a possible porosity ordering. While the optical transmission is the high in the visible and near infrared spectral range as per mentioned above, the films are highly absorbing in the UV part with an average transmission less than 1%. From the wavelength cut-off ($\lambda_{\text{cut-off}}$) (Figure 33), it is possible to deduce therefore the effective optical bandgap $E_g^{\text{opt}} = hc / \lambda_{\text{cut-off}}$ with h and c , the Planck's constant and the celerity of light. $\lambda_{\text{cut-off}}$ is about 324.9, 310.6, 323.2 and 315.0 nm for TiO₂-A, TiO₂-A DIL, TiO₂-B and TiO₂-B DIL, respectively. The corresponding bandgap values are therefore 3.82, 3.99, 3.84 and 3.9 eV for TiO₂-A, TiO₂-A DIL, TiO₂-B and TiO₂-B DIL, respectively. These values which are larger than the bulk anatase value are effective values as the films are porous and that the optical absorption in the UV spectral region is due to the interband transition. One should note that recent studies on porous nano-scaled TiO₂ showed such a bleu shift of the optical bandgap relatively to the bulk anatase of about 3.2 eV, i.e. 380nm in terms of wavelength. More precisely, Bavykin et al have showed recently that nanotubes of TiO₂ follow a 2-D optical behavior due to the large effective mass of the charge carrier and the electronically isolated layered structure [Bav-2004]. It was concluded that the electronic structure of the TiO₂ nanotubes is very close to TiO₂ nanosheets. Sakai et al [Sak-2004] have estimated the bandgap of the TiO₂ nanosheets as 3.8 eV, which corresponds to a wavelength of 326 nm, based on electrochemical and photoelectrochemical investigations. These values are closer to the experimental deduced ones. Moreover, recent density functional theory studies have suggested that

the bandgap energy of TiO₂ nanosheets i.e. open structures is larger than that of bulk anatase due to a quantum size effect in a 2-D structure.

Table 5: Optical data for samples TiO₂-A, TiO₂-B, TiO₂-B DIL.

	α	T_{Min}	T_{Max}	n_s effective	n
TiO ₂ -BDIL					
	411	65.88	81.68	1.633	1.5104
	484.16	68.13	81.92	1.632	1.508
	586.25	70.38	82.38	1.631	1.507
	770.8	73	80.98	1.629	1.505
	971.6	71.52	78.6	1.629	1.504
	1666.6	68.35	65.65	1.623	1.498
TiO ₂ -B					
	365.7	59.37	72.37	1.634	1.511
	438.25	67.07	74.81	1.629	1.505
	637.15	68.83	80.33	1.631	1.507
	1681.45	75.63	81.45	1.628	1.503
TiO ₂ -ADIL					
	328.87	44.1	66	1.647	1.526
	336	72.62	80.2	1.629	1.505
	544	61	78	1.635	1.516
	1678.27	75.057	77	1.626	1.501

Table 6: Cut-off wavelengths of different meso-porous nanostructured TiO₂ films after calcination.

Samples	Cut-off wavelength $\lambda_{Cut-off}$ (nm)	Optical bandgap E_g^{Opt} (eV)
GIB-14A	324.90	3.82
GIB-14Adil	310.59	3.99
GIB-14B	323.20	3.84
GIB-14Bdil	315.00	3.90

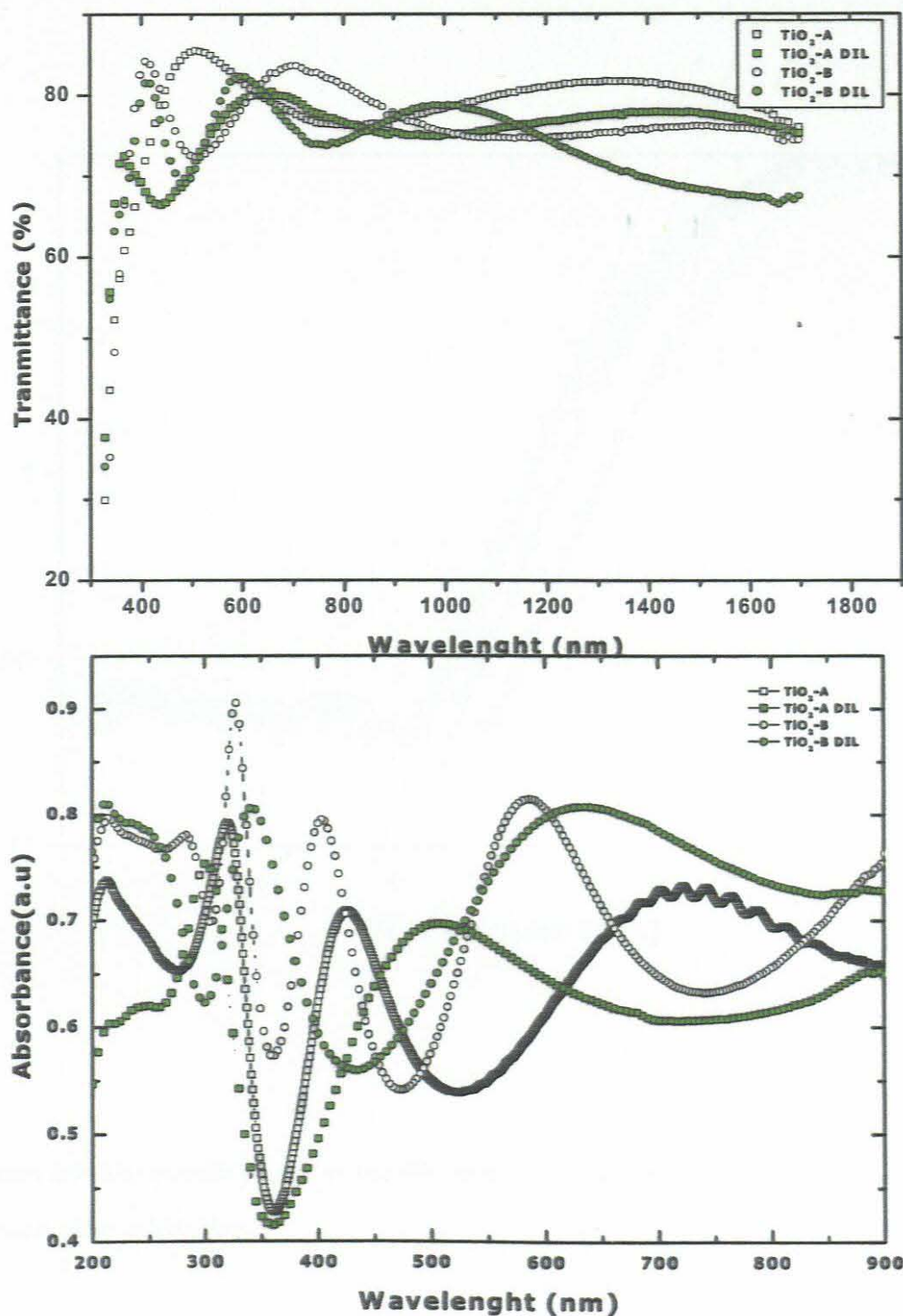


Figure 32: Room temperature UV-VIS-NIR normal incidence (a) optical transmission and (b) diffuse scattering spectra of the different meso-porous nanostructured TiO_2 films samples after calcination.

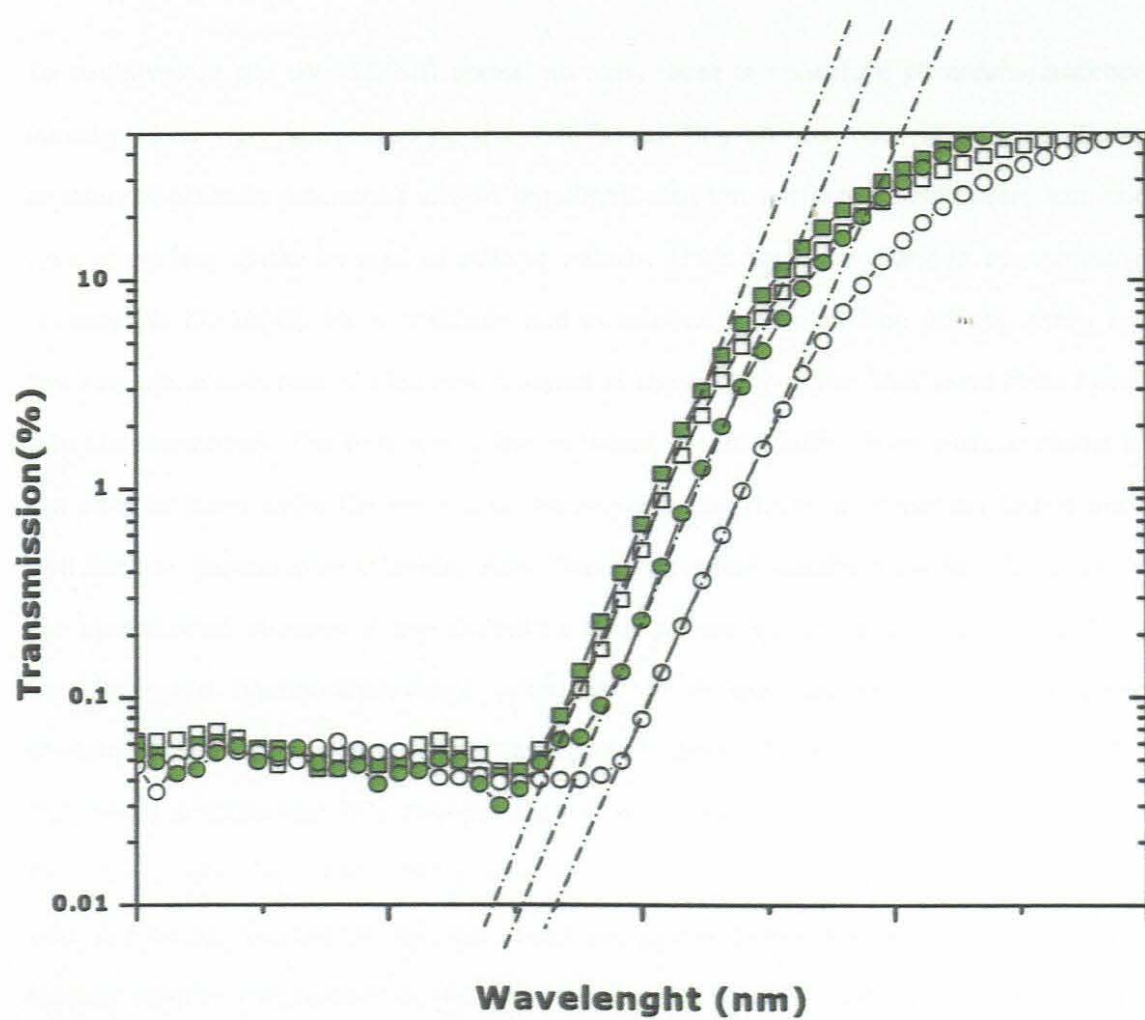


Figure 33: Wavelength cut-off of the different meso-porous nanostructured TiO_2 films samples after calcination.

5.2.4 Defects and photoluminescence properties

To complement the UV-VIS-NIR optical studies, room temperature photoluminescence investigations were conducted on the 4 different TiO_2 porous meso-structures. These photoluminescence properties should shedlight onto the surface stoichiometry and the type of surface states as well as volume defects which could be changed by annealing process [W Zh-2000]. More precisely and in relation to the surface effects, there are two relaxation channels of electrons trapped at the surface states that need to be taken into considerations. The first one is the radiative recombination from surface states to the valence band while the second is the nonradiative decay at imperfect lattice sites and surface stoichiometric layers. Both these relaxation channels could take place in the investigated samples if one considers their porous structure. In the case of TiO_2 , their reported photoluminescence properties of in the literature, exhibit a broad photoluminescence response related to defects is generally present in amorphous TiO_2 , TiO_2 single crystals and TiO_2 nanoparticles in their anatase or brookite forms but not in the rutile phase [Dit- 2000]. More precisely, recent studies revealed that these defects that are being responsible for the electronic states below the absorption edge are located at/near the surface of the TiO_2 nanoparticles [Dit- 2000]. In the case of the anatase form, the photoluminescence spectra are attributed to three kinds of physical origins: self-trapped excitons [Ten-1989, Kaj-1998], oxygen vacancies [Ten-1998, Ten-1998] and surface states i.e. defects [Ten-1989]. In this later case, the foremost surface states are oxygen vacancies or Ti^{4+} ions adjacent to O vacancies [Ten-1989]. The self trapped excitons localized on TiO_6 octahedra are the photoluminescence source in the single crystals and anatase nanoparticles forms.

Figure 34 reports the room temperature photoluminescence spectra of the different samples. These PL measurements were recorded on a Hitachi 850 unit-Japan using an

argon laser source at an excitation wavelength of 476 nm in the standard normal incidence. The different photoluminescence spectra exhibit an identical trend which consists of 3 well separated bands with approximately the same intensities. Their maxima positions are within the following spectral range: 401-407, 520-529 and 705-715 nm respectively. The violet photoluminescence within 401-407 nm compares satisfactorily with the observed values by Kajihara et al and that of lei et al [Lei-2001] which are about 412 and 425 nm. Likewise, as this band seems not to change with the 4 different samples, this could indicate that it likely originates from the intrinsic states rather than the surface states. Hence, one could conclude as in the case of Lei et al, that this 401-407 nm first photoluminescence band should be assigned to self-trapped excitons localized on TiO_6 octahedra.

The 520-529 nm blue band compares with the ones observed by Kajihara et al and Wu et al [J Wu-2002] at about 460 and 530 nm. As, it was established by the mentioned authors whereby this blue band is associated to shallow traps identified with oxygen vacancies below the conduction band, the 520-529 nm band observed in this case should be attributed to oxygen vacancies. One could mention the related results of Forss et al [For-1993] in which this second band was attributed rather to surface states and those of Redmond et al [Red-1993] attributed to surface trap states. In this latter work, the traps were identified with Ti atoms adjacent to oxygen vacancies at the surface. The last 705-715 nm band could be associated to surface states in correlation with the PEO previously occupied surface space. Before calcinations, the PEO chains and titania coexisted in one domain and we speculate that the PEO affected the titania surface. It is therefore assigned the band at 710nm to defects in the surface state of titania. Zaicheng Sun has shown that the photoluminescence intensity increases after calcination. However, to some extent the intensity of the spectra is further increased by removing the polymer template as compared to the films retaining the polymer matrix.

This tends to agree with the model we used where PEO chains and Titania particles coexists in one intermixed domain, in that case the intermixing of PEO chains leads to a quenching of PL.

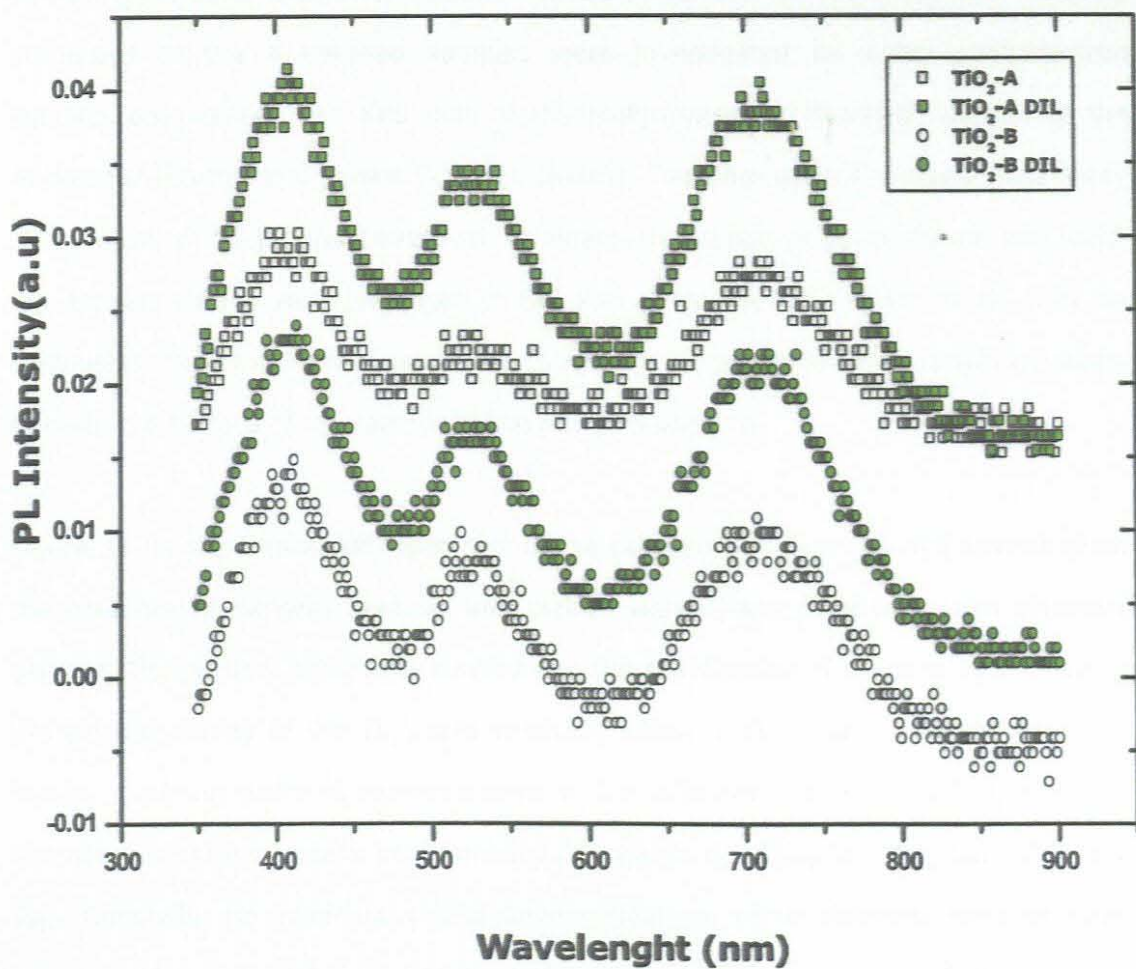


Figure 34: Room temperature photoluminescence spectra of the different TiO_2 mesoporous nanostructures; Excitation laser wavelength $\lambda = 476 \text{ nm}$.

5.2.5 Bonding chemical and electronic properties

To complete the photoluminescence studies, surface composition and bonding properties of the 4 calcined samples were investigated by X-ray photoelectron spectroscopy «XPS». The XPS unit of the Multi-functional Materials Division of the National Institute for Materials Sciences (NIMS), Tsukuba-Japan was used. $AlK\alpha$ X-ray (1486.6 eV) at 15 kV and 100W with an energy resolution of about 0.8 eV was used. The binding energy was referenced to Si_{2p} line at the standard value of 99, 0 eV for calibration. The films were sputtered for about 40 seconds with 15 kV argon ion beam to clean the surface of the sample before any XPS analysis.

Figure 35 reports typical XPS spectrum of the calcined samples. The XPS spectra show the presence of oxygen, titanium and carbon without any additional extra elements present. The primary parameter studied was the coordination of titanium by measuring the binding energy of the Ti_{2p3} core electron, which is 457.1 eV. Figure 35 depicts a typical spectrum which is representative of the different meso-porous TiO_2 samples. The observed major intense peaks are the followings: C_{2p} , Ti_{2p3} , O_{1s} , Ti_{2s} , O_{KLL} , Ti_{LMM} and C_{KLL} . Generally, no additional peaks corresponding to other elements were detected confirming the chemical purity of the obtained nano-scaled mesoporous Titania.

The binding energy of the $Ti_{2p}^{3/2}$ is located at about 459.2 eV, close to the value of anatase [Mur-1975]. The slight red shift of such a peak could indicate a change of the micro-environments for the titanium atoms which could be induced to the interaction of TiO_2 sites located on the surface of the meso-porous backbone. In terms of chemical stoichiometry of the titania meso-porous nanostructures, this can be deduced via the relative intensities of the O and Ti XPS peaks. More specifically, it can be determined from the ratio of the O_{1s} and Ti_{2p} values once corrected with their sensitivity factors.

The two contributions result from the splitting of the 2p level related to the spin-orbit coupling. As mentioned above, the $2p^{3/2}$ binding energy is about 458.7 eV while the $2p^{1/2}$ is located at a higher energy of 5.7 eV. These values which are closer to the observed ones are characteristic of the Ti^{4+} ions in the TiO_2 structure being it in its powder, monocrystal or thin films configuration as per reported in the literature by the following researchers [Wag-1979, Mui-1979, Stak-1993, Pee-1998, Gui-2002]. Moreover, the symmetrical form of the peaks substantiates the absence of reduced species of Ti^{3+} and Ti^{2+} which are normally detected at lower energy values of 1.7 and 4.3 eV as reported by Stakheev et al. The corrected ratio is generally about 0.93 ± 0.2 confirming the chemical stoichiometry of the different meso-porous TiO_2 samples.

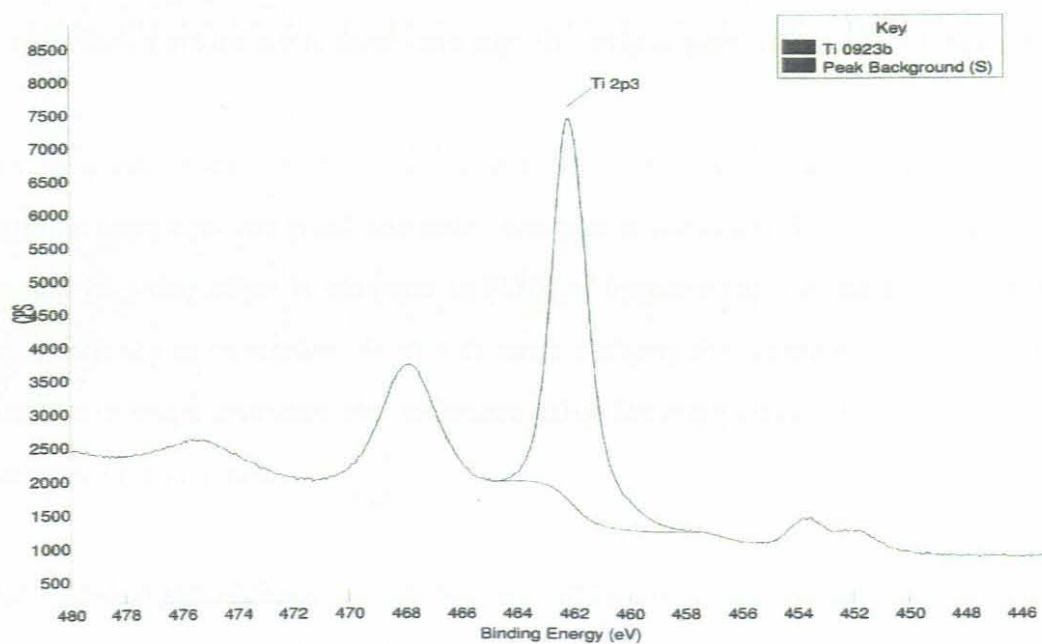
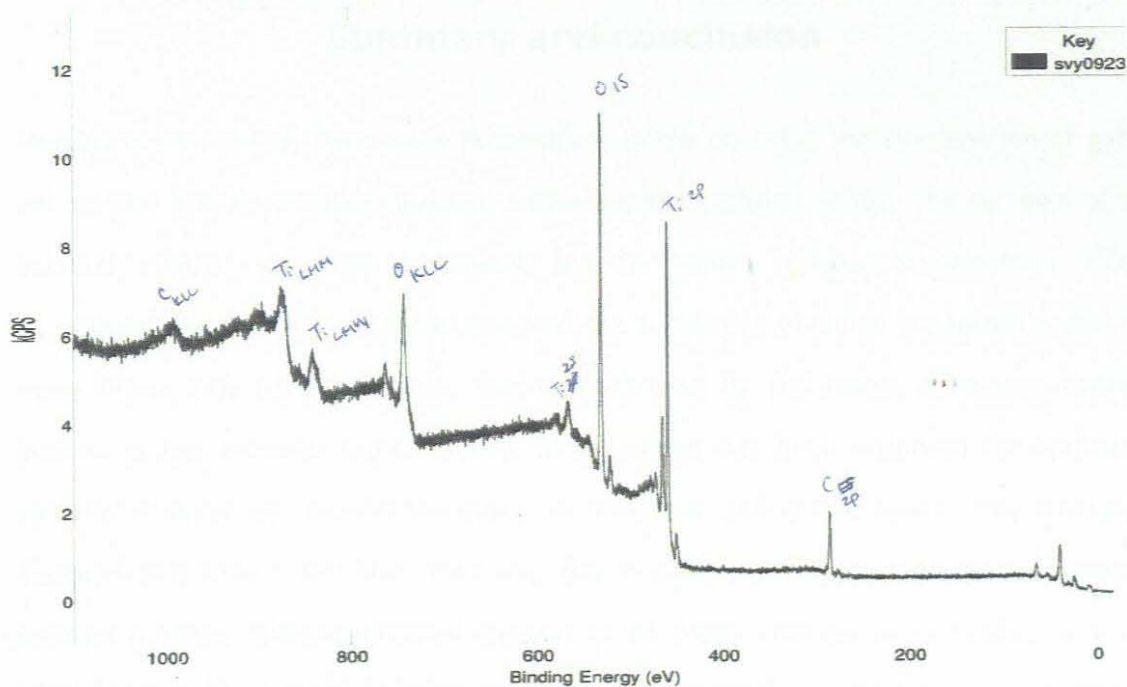


Figure 35: Typical X-ray photoelectron spectroscopy spectra of one of the TiO_2 mesoporous nanostructure (TiO_2 -A DIL).

Summary and conclusion

Mesoporous nano-TiO₂ films were successfully prepared using the combination of sol-gel method and Evaporation Induced Self-Assembly (EISA) method. The removal of a polymer matrix via heat treatment led to highly ordered mesoporous TiO₂ nanostructures. The XRR analysis revealed the formation of highly organized ordered mesoporous TiO₂ nanostructures. This is confirmed by the Bragg diffraction peaks located at low incident angle. Narrow Bragg peaks has been observed for calcined samples whereas un-calcined samples only exhibited wide Bragg peaks. This strongly suggests that before and after calcining, the mesoporous TiO₂ nanostructures remain ordered but the calcined samples showed to be much ordered as compared to un-calcined ones. The grazing incident small angle x-ray scattering indicated the presence of BCC *Im3m* structure with a lattice parameters of 'a' = 9.1 nm i.e d₁₁₀ of about 6.3nm. These values are in consistent with the ones obtained from XRR measurements.

Only anatase peaks with the most intense [101] peak could be observed from XRD patterns except for the small shoulder peak that is persistent for all 4 samples located around 24.8 deg which is assigned to [120] of Brookite nano-crystals. The Diffraction peaks seemed to be weaker for all 4 samples implying the presence of imperfect lattice site. The average crystallite size estimated using Scherer's equation was found to range between 12 and 15nm.

Optical properties of these films were recorded by doing both transmittance and diffuse reflectance measurements. The transmittance measurements revealed that the mesoporous TiO₂ films deposited onto the FTO coated glass substrate are highly transparent, where transmittance T_s ranges between 70-85%. It was then concluded that the investigated mesoporous TiO₂ are highly transmitting in the visible and near

infra-red regions and highly absorbing in the UV region with an average transmission less than 1% which is due to the interband transition. Since optical transmittance exhibit optical interference fringes patterns which are related to their limited film thickness, both the refractive indexes and film thicknesses of the mesoporous TiO₂ films were therefore estimated following the method reported by Manifacier. The average value of the refractive index for these mesoporous TiO₂ films was found to be around 1.5 which is far less than that of bulk anatase TiO₂ 2.56. This strongly suggests the investigated TiO₂ films exhibit very high porosity architecture of about 76%. The very low diffuse reflectance exhibited by all samples confirms a possible porosity ordering. The bandgap values were found to be less than that of bulk anatase TiO₂ which is effective in this regard since the films are porous.

The PL properties were also studied by using an Argon laser source at an excitation wavelength of $\lambda = 476$ nm. The PL emission spectra showed the significant similar characteristic for all 4 calcined samples and their PL intensities are almost the same. The first PL band around 401-407 is attributed to self-trapped excitons localized on TiO₆ octahedra. This is followed by a blue band around 401-407 which is assigned to oxygen vacancies. The final band observed at 710nm could be associated with defects in the surface state of Titania. It was therefore concluded that the PEO chains and Titania nanoparticles coexists in the intermixed domain which then led to intermixing of PEO chains as a result of quenching of PL.

These PL measurements were confirmed by XPS analysis where only Oxygen, Titanium as well as Carbon could be observed. The chemical impurity of the nano-sized mesoporous TiO₂ was confirmed by the presence of the major intense peaks such as C_{2p}, Ti_{2p3}, O_{1s}, O_{KLL}, Ti_{KLL}, and C_{KLL}, no other peaks corresponding to the other elements could be detected.

References

- [A Ba-2005] A. Barnard and L. A. Curtis, Nano Letters, Vol.5, p.1261 (2005)
- [A Bar-2005] A. Barnard, P. Zapol, and L. A. Curtiss, Surface Science Vol. 582, p. 173 (2005)
- [Ada-2004] Motonari Adachi, Yusuke Murata, Jun Takao, Jinting Jiu, Masaru Sakamoto, and Fumin Wang, J.Am. Chem. Soc., Vol.126, pp.14943-14949 (2004)
- [Alb-2002] P.C.A. Alberius, K.L. Frindell, R.C. Hayward, E.J. Kramer, G.D. Stucky, and B.F. Chmelka, Chem. Mater., Vol.14, p. 3284 (2002)
- [Aso-2007] K.Asoagoe, Y. Suzuki, S. Ngamsinlapasathian, and S.Yoshikawa J.Phys.:Conference.Series Vol. 61 pp. 1112-1116(2007)
- [Bar-2005] A. Barnard, P. Zapol, and L. A. Curtiss, Journal of Chemical Theory and Computation Vol. 1,p.107 (2005)
- [Bav-2004] D.V Bavykin, V.N Parmon, A.A Lapkin, F.C Walssh, J. Mater.Chem, Vol. 14, 3370 (2004)
- [Bec-1992] J.S. Beck, J.C Vartuli, W.J Roth, M.E Leonowicz, C.T Kresge, K.D Schmitt, C.T-W Chu, D.H Olson, E.W Sheppard, S.B McCullen, J.B Higgins, and J.L Schlenker, JACS Vol. 114, p.10834 (1992)
- [Bel-2006] Emmanuelle Lancelle-Beltran, Philippe Prené,* Christophe Boscher, Philippe Belleville, Pierrick Buvat, and Clément Sanchez, Adv. Mater., Vol.18, pp.2579–2582(2006)
- [Big-2006] T.P Bigioni, X.M Lin, T.T Nguyen, E.I Corwin, T.A Witten, H.M Jaeger, Nat. Mater.Vol. 5, p.265 (2006)
- [Bre-1961] F.P. Bretherton, J. Fluid Mech., Vol. 10, p.166, (1961)
- [Bre-2006] T. Brezinsky, M. Groenewolt, A. Gibaud, N. Pinna, M. Antonietti, B.M. Smarsly, Advanced Mater. Vol. 28, pp.2260-22263 (2006)

- [Bri-2003] C. Jeffrey Brinker, B. Smarsly, G. Garnweitner and R. Assink, Progress in Organic Coatings, Vol. 47, Iss.3-4, pp. 393-400 (2003)
- [Bur-1988] J. P. Burelbach, S.G. Bankoff and S.H Davis, J. Fluid Mechanics Digital Archive, Vol. 195, pp. 463-494 (1988)
- [Cac-2002] Paola Cacciafesta , Keith R.Hallam, Caroline A. Oyedepo, Andrew D.L.Humphris, and Mervyn J.Miles, and Klaus D. Jandt.Chem.Mater., Vol. 14, pp. 777-789 (2002)
- [Can-2003] Giovanni Cangiani, 2003
- [Cha-1997] Charlton G, Howes P.B, Nicklin C.L, Steadman P, Taylor J.S.G, Muryn C.A, Harte S.P, Mercer J, McGrath R, Norman D, Turner T.S, Thorntong G, Physical Review Letters, Vol. 78,pp.495-498 (1997)
- [Che-2008] Wei Chen, Yi Geng, Xiao-Dan Sun, Qiang Cai, Heng-De Li and Duan Weng Microporous and Mesoporous Mates., Vol. 111, Iss. 1-3, pp. 219-227 (2008)
- [Cho-1989] T. Choudhury, S.O. Saied, J.L. Sullivan and A.M. Abbott, J. Phys. D.22, p.1185 (1989)
- [Con-1996] Contescu C, Popa V.T, Schwarz J.A, Journal of Colloidal and Interface Science, 180, pp.149-161 (1996)
- [Cre-2003] E.L. Crepaldi, G.J. de A.A. Soler-Illia, D. Grosso, F. cagnol, F. Ribot and C. Sanchez, J.Amer. Chem. Soc. Vol. 125, p.9770 (2003)
- [D Qu-2002] D. Qu, E. Rame & S. Garoff, J. Appl. Phys.,Vol. 14, p.1154 (2002)
- [Das-1993] S. Das Gupta, J.A. Schonberg & P.C. Wayner, J. Colloid. Interf. Sci.Vol.157, p.332 (1993)
- [Deb-1998] S.K Deb, R. Ellingson, S. Ferrere, A. J Frank, B.A Gregg, A. J Nozik, N. Park, and G. Schlichthorl. National Renewable Energy Laboratory (NREL) (1998)

- [Dee-1997] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel and T.A. Witten, *Nature*. 389, p.827, (1997)
- [Dee-2000] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel and T.A.Witten, *Phys. Rev. E*.62, p.756, (2000)
- [Die-1998] Diebold U, Lehman J, Mahmoud T, Kuhn M, Leonardelli G, Hebenstreit W, Schmid M, Varga G, *Surface Science*, Vol. 411, pp.137-153 (1998)
- [Dit- 2000] TH. Dittrich *Phys.Stat.Sol "a"* Vol. 182, p.447 (2000)
- [Dit-2000] T.H Dittrich, *Phys.Stat.Sol "a"* Vol. 182, pp.447 (2000)
- [Dor-1997] Kluwer Academic Publishers, Dordrecht, 1997
- [Fan-2008] Xiaoxing Fan, Tao Yu, Ying Wang, Jing Zheng, Ling Gao, Zhaosheng Li, Jinhua Ye and Zhigang Zou' *Applied Surface Science*, Vol. 254, Iss.16, pp. 5191-5198 (2008)
- [Fin-2001] Finnie K.S, Cassidy D.J, Bartlett J.R, Woolfrey J.L, *Langmuir*, Vol. 17, pp.816-820 (2001)
- [Flo-2007] Ismael .C. Flores, Jilian Nei de Freitas, Claudia Longo, Marco-Aerelio De Pauli, Herbert Winnischofer, Ana Flavia Nogueira, *J.Photochem. & Photobiol.A:Chem*.Vol. 189 153-160 (2007)
- [For- 1993] L. Forss & M. Schubnell, *Appl. Phys. B*.56, p.363 (1993)
- [Fre-2005] J.B. Freund, *Phys. Fluids* Vol.17, p.22104 (2005)
- [Fri-1999] L.J.D. Frink & F. van Swol, *Langmuir* Vol.15, p.3296 (1999)
- [Gle-2005] M. Gleiche et al, *Nture*, Vol.403, p.173 (2000)
- [Goe-2003] A. Goetzberger,C. Hebling, and H. Werner Schock *Mater.Scie. & Engin. R40* (2003)
- [Gon-1991] D. Gonbeau, C. Guimon, A. Levasseur, G. Meunier, R. Dormoy, *Surf. Sci.* Vol. 254, p.81 (1991)
- [Gon-1996] Reinaldo J. Gonzalez, 1996
- [Gra-2005] Michael Gratzel, *Chem. Lett.*, Vol.34, No.1, pp.8-13(2005)

- [Gro-2004] D. Grosso, F. Cagnol, Galo J de A, A. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, and C. Sanchez. *Adv. Funct. Mater.* Vol.14, No.4, pp 309-322 (2004)
- [Gros-2004] D. Grosso, F. Babonneau, C. Sanchez, G.J. de A.A. Soler-Illia, E.L. Crepaldi, P.A. Albouy, H. Amenitsch, A.R. Balkenende and A. Brunet-Bruneau, *Journal of Sol-Gel Science and Tech.*, Vol. 26, No.1-3, pp. 561-565 (2004)
- [Gui-2002] J. Guillot, Thesis, University of Bourgogne (2002)
- [H Ko-2006] H. Ko and V.V. Tsuruk, *nanolett.*, Vol. 6, p. 1443 (2006)
- [Had-1996] Hadjivanov K.I, Klissurski D.G, *Chemical Society Reviews*, pp.61-69 (1996)
- [Han-2000] Y.J. Han, JM Kim and GD Stucky, *Chem. Mater.*, Vol. 12, p.2068 (2000)
- [Har-2001] Kohjiro Hara, Kazuhiro Sayama, Yasuyo Ohga, Akira Shipo, Sadaharu Suga, and Hironori Arakawa. *Chem. Commn.* pp. 569-570 (2001)
- [Heb-2000] Hebenstreit W, Ruzycki N, Herman G.S, Gao Y, Diebold U, *Physical Review*, B62, R16334-R16336 (2000)
- [Hen-2004] M. J. Henderson, A. Gibaud, J.-F. Bardeau and J. W. White, *Advanced Mater.*, Vol. 14, Iss. 4, pp. 309 – 322 (2004)
- [Heu-2001] A.J. Heur & L. Steinberg, *Granular Matter*.Vol. 3, p.19 (2001)
- [Hin-2001] A. Hinsch, J. M. Kroon, R. Kern, R. Sastrawan, A. Meyer, I. Uhlendorf, J. Ferber, *Prog. Photovolt.: Res. Appl.* Vol. 9, pp. 425-438 (2001)
- [Hir -1999] T. Hirai, H. Okubo, and I. Komasaawa, *J. Phys. Hem.* B103, p. 4228 (1999)
- [Hua-2000] M.H. Huang, A. Choudrey, and PD Yang, *Chem. Comm.*, 1063 (2000).
- [Hua-2005] J. Huang, F. Kim, A.R. Tao, S. Connor, and P. Yang, *Nat. Mater.* Vol. 4, p.896 (2005)
- [Hur-2001] A.J. Hurd & L. Steinberg, *J. Mater.*, Vol. 3, pp. 1434-5021 (2001)

- [Hwa-2006] U-Hwang Lee, Hae Seong Lee, Sun Wen, Sun-il Mho and Young-Uk Kwon, *Microporous and Mesoporous Materials*, Vol. 88, Issues 1-3, pp. 48-55 (2006)
- [Imh-1997] A. Imhof & D.J. Pine, *Nature*, Vol. 389, p.948 (1997)
- [J He-2002] J. He, G. Benko, F. Korodi & V. Sundstrom, *J. Am. Chem. Soc.* Vol. 124, p. 4922 (2002)
- [J Wu-2002] J. M. Wu, S. Hayakawa, K. Tsuru & A. Osaka, *Scripta . Mater.*Vol. 46, p.101 (2002)
- [Jia-2004] Dianlu Jiang, School of Environmental and Applied Sciences, June 2004
- [Jon-1971] P. Jones and H.J. Hockey, *Journal of the Chemical Society: Faraday Transactions*, Vol. 67, pp.2669-2685 (1971)
- [Kaj-1998] K. Kajihara, K. Nakanishi, K. Tanaka, K. Hirao & N. Soga, *J. Am. Ceram. Soc.*Vol.81, p.2670 (1998)
- [Kal-2006] A.M. Kalsin, M. Fialkowski, S.K Smoukov, K.J.M Bishop, and B.A Grzybowski, *Science*, Vol. 312, p.420 (2006)
- [Kar-2002] B.Karunagaran, R.T.Rajendra Kumar,D.Mangalaraj, Sa. K. Narayandass, and G.MohanRao .*Cryst. Res.Technol.* Vol. 37, pp.1285-1292 (2002)
- [Kar-2004] I. Kartini, P. Meredith, J. C. Diniz da Costa, J. D. Riches and G. Q. M. Lu, *Current App. Phys.*, Vol. 4, Iss.2-4, pp.160-162 (2004).
- [Kua-2007] Daibin Kuang, Cedric Klein, Seigo Ito, Jacques-E.Moser, Robin Humphry-Baker, Nick Evans, Francine Duriaux, Carole Gratzel, Shaik M.Zakeerruddin, and Michael Gratzel, *Adv. Mater.*, Vol. 19, pp. 1133-1137 (2007)
- [L Fu-2007] L.J. Fu, T. Zhang, Q. Cao, H.P. Zhang and Y.P. Wu, *Electrochemistry Comms.* Vol. 9, Issue 8, pp. 2140-2144 (2007)

- [L Hu-2007] Linhua Hu, Songyuan Dai,* Jian Weng, Shangfeng Xiao, Yifeng Sui, Yang Huang, Shuanghong Chen, Fantai Kong, Xu Pan, Linyun Liang, and Kongjia Wang, *J. Phys. Chem. B* 111, pp.358-362 (2007)
- [L Zh-2004] Lili Zhao, Yun Yu, Lixin Song, Meiling Ruan, Xingfang Hu and André Larbo, *Applied Catalysis A: General*, Vol. 263, Issue 2, pp. 171-177, (2004)
- [Laz-2000] Lazzeri M, Vittadini A, Selloni A, *Physical Review*, B65, (2000)
- [Lee-2008] C.H. Lee, Y. Lu & A.Q. Shen, *Phys. Fluids*, (2008)
- [Lei-2001] Y. Lei & L. D. Zhang, *J. Mater. Res. Vol. 16*, p.1138 (2001)
- [Lin-2001] Lindan P.J.D, Harrison N.M, *Surface Science*, 2001, 479, L375-L381
- [Lin-2001] P.J.D. Lindan and N.M. Harrison, *Surface Science*, Vol. 479, pp.L375-L381 (2001)
- [Lin-2005] Y. Lin et al, *Nature*, Vol. 434, p.55 (2005)
- [Liu-2005] Kesong Liu, Milin Zhang, Keying Shi and Honggang Fu, *J. Materials Lett. Vol.5*, pp.62-64 (2005)
- [Lun-2006] M. J. Lundqvist, M. Nilsing, S. Lunell, B. Åkermark and P. Persson, *J. Phys. Chem. B* 110, 20513 (2006)
- [Mad-2006] G. Madras & B. J. McCoy, *J. Crys. Growth*, Vol. 286, Iss.1, pp.131-136, (2006)
- [Man-1976] J.C. Manificier, J. Gasiot, J.P.Fillard, *J. Phys. E* 9, p.1002 (1976)
- [Man-1976] J.C. Manificier, J. Gasiot, J.P.Fillard, *J. Phys. E* 9, p.1002, (1976)
- [Moo-1980] S. Moosman & G. M. Homsy, *J. Colloid. Interf. Sci. Vol. 73*, p.212 (1980)
- [Mor-2006] Gobal .K Mor, Omman.K. Varghese, Maggie Paulose, Karthik Shankar and Craig.A. Grimes, *Solar Materials & Solar Cells*, Vol. 90 pp 2011-2075(2006)

- [Mur-197] M. Murato, K. Wakino and S. Ikeda, J. Electron. Spectrosc. Relat. Phantom. Vol.6, p.459 (1975)
- [Mur-1995] Murakoshi, Kei, Kano, Gentaro Wada, Yuji Yanagida, Shozo, Miyazaki, Hiromitsu, Matsumoto, Masamitsu, Murasawa, Sadao Journal of Electroanalytical Chemistry Vol.396 (1995)
- [Nga-2006] Supachai Ngamsinlapasathian, Sorapong Pavasupree, Yoshikazu Suzuki, Susumu, Yoshikawa, Solar Energy Materials & Solar Cells, Vol.90, No.18 (2006)
- [Nil-2006] M. Nilsing, S. Lunell, P. Persson and L. Ojamäe, Surface Science 582, 49 (2005)
- [Oni-1994] Onishi H, Iwasawa Y, Surface Science Report, 1994, 313, L783-L789
- [Pan-2007] X. Pan, S-Y. Dai, and K.J. Wang, Chiniese J. Chem. Vol. 25, Iss. 11, 1601 (2007)
- [Par -2000] H. Parala, H. Winkler, M. Kolbe, A. Wohlfart, R.A Fisher, R.Schmechel, J. von Seggern, Adv. Mater. Vol.12, 1050 (2000)
- [Pav-2007] Sorapong Pavasupree, Supachai Ngamsinlapasathian, Yoshikazu Suzuki and Susumu Yoshikawa, J. Sol.Mech. & Mater. Engin. Vol.1, No.4 (2007)
- [Pee-1998] S. Peetigny, H. Mostefa-Sba, B. Domenichini, E. Lesniewska, A. Steinbrunn, and S. Bourgeois, Surf. Sci., vol. 410, pp. 250–257 (1998)
- [Per-2002] P. Persson, R. Bergström, L. Ojamäe and S. Lunell, Advances in Quantum Chem. 41, 203 (2002)
- [Pri-1971] Primet M, Pichat P, Mathieu M.V, Journal of Physical Chemistry, Vol. 75, pp.116-120 (1971)
- [Rab-2003] E. Rabani, D.R Reichman, Ph.L. Geissler and L. E Brus, Nature Vol. 426, p.271 (2003)

- [Ram-1994] M. Ramamoorthy, D. Vanderbilt and R.D. King Smith, *Physical Review*, pp.16721-16727 (1994)
- [Ram-1994] Ramamoorthy M, Vanderbilt D, King-Smith R.D, *Physical Review*, B49, pp. 16721-16727 (1994)
- [Ran-2000] S.E. Rankin, L.J Kasehagen, A.V McCormick and C. W Macosko, *Macromolecules*. Vol. 33, p.7639 (2000)
- [Ran-2005] Jeffrey Lymn Rankinen, 2005
- [Rar-1990] J. Ratulowski and H.J Chang, *Fluid. Mech.* Vol. 210, p.303, (1990)
- [Rat-2007] Jiří Rathouský, Dina Fattakhova Rohlfing, Michael Wark, Torsten Brezesinski and Bernd Smarsly, *Thin Solid Films*, Vol. 515, Iss. 16, pp.6541-6543 (2007)
- [Red-1993] G. Redmond, D. Fitzmaurice & M. Gratzel, *J. Phys. Chem.*97, p.6951 (1993)
- [Rot-2000] P.W.K. Rothmund, *Natl. Acad. Sci. USA*, Vol. 97, p.984 (2000)
- [Rus-1985] K. J. Ruschak, *Ann. Rev. Fluid Mech.*Vol. 17, p.65 (1985)
- [S Zh-2004] Shengmao Zhang, Benfang He, Zhijun Zhang, Hongxin Dang, Weimin Liu, and Qunji Xue, *Chemistry Letts.*, Vol. 33, No. 11 pp. 1498-1500 (2004)
- [Sak-2004] N. Sakai, Y. Ebina, K. Takada and T. Sasaki, *J. Am. Chem. Soc.* Vol. 126, pp. 5851-5858 (2004)
- [Say-2001] A. Sayari, S. Hamoudi, *Chem. Mater.* Vol. 13, 3151, (2001)
- [Sch-2004] M. Linke-Schaetzel, A.D Bhishe, H.Gliemanm, T Koch, T.Schimmel, and T.S Balaban, *Thin Solid Films* Vol. 16, pp. 451-452 (2004)
- [Sck-1997] Shklover V, Nazeeruddin M.K, Zakeeruddin S.M, Barbe C, Kay A, Haibach T, Steurer W, Hermann R, Nissen H.U, Gratzel M, *Chemistry of Materials*, Vol. 9, pp.430-439, (1997)

- [Scr-1962] L.E. Scriven in Physico-chemical Hydrodynamics, Englewood Cliffs: Prentice Hall Inc.(1962)
- [Sol-2002] G. J. de A. A. Soler-Illia, A. Louis, and C. Sanchez, Chem. Mater., Vol. 14, pp.750 -759 (2002)
- [Sol-2003] Soller-Illia, G.J. de A.A. Soller-Illia, E.L. Crepaldi, D. Grosso and C. Sanchez, Curr. Opin. Colloid Interface Sci. Vol. 8, p. 109 (2003)
- [Som-1998] P.M Sommeling, M.Spath, and J.A.M van Roosmalen, Proc. 2nd World Conf. and Exhibition on Photovoltaic Solar Energy Conversion (WCPEC-02), pp. 288(1998)
- [Son-2006] S.S Soni, M.J Henderson, J.F Bardeau, J.W White, and A Gibaud
- [Son-2008] S.S Soni, M.G Henderson, J.F Bardeau, and A Gibaud, Adv.Mater. 9999, pp.1-6 (2008)
- [Spa-1997] M. Spath, P.M. Sommeling, J. Wienke & O. Kohle, 14th EPVSEC, ECN RX-97 032 (1997)
- [Srd -1998] V. I. Srdanov, I. Alxneit, G.D Stucky, C.M Reaves, S.P Denbears, SP, J. Phys. Chem. B Vol. 102, 3341 (1998)
- [Sta-1993] A. Y. Stakheev, E. Shpiro, and J. Apijok, J. Phys. Chem., vol. 97, pp. 5668–5672 (1993)
- [T Ma-2005] Tingli Ma, Morito Akiyama, Eiichi Abe, and Isao Imai, Nano Lett., Vol.5, No.12 (2005)
- [Tan-2006] Bing Tan and Yiyang Wu, J.Phys.Chem.B, Vol. 110, pp. 15932-15938 (2006)
- [Ten-1989] P. Tengvall, I. Lundstrom, L. Sjobqvist, H. Helwing, L.M. Bjurstein, Biomaterials, Vol. 10, p.166 (1989)
- [Ten-1998] P. Tengvall, PhD thesis, Linkoping University, Sweden (1998)

- [Thu-2000] T. Thurn-Albrecht, J.Schotter, C.A Kastle, N. Emley, T.Shibauchi, L. Krusin-Elbaum, K. Guarini, C.T Black, M.T Tuominen, T.P Russell, Science, Vol. 290, p. 2126 (2000)
- [Tsu-2004] V.V Tsukruk, H. Ko, and S. Peleshanko , Phys. Rev. Lett. Vol. 92, 065502 (2004)
- [Uet-2000] Uetsuka H, Sasahara A, Onishi H, Japanese Journal of Applied Physics, Vol. 39, pp. 3769-3772 (2000)
- [Vit-1998] Vittadin A, Selloni A, Rotzinger F.P, Gratzel M, Physical Review Letters, Vol. 81, pp. 2954-2957 (1998)
- [W Zh-2000] W.F Zhang, M.S Zhang, and Z. Yin Phys. stat. sol. (a) Vol. 179, p. 319, (2000)
- [W Zha-2000] W.F Zhang, M.S Zhang, and Z. Yin Phys.stat.sol. "a" 179, pp 319 (2000)
- [Wag-1979] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg, Handbook of X-ray Photoelectron Spectroscopy. Perkin-Elmer Corporation, Physical Electronics Division (1979)
- [Wan-2004] Peng Wang, Cedric Klein, Jacques-E. Moser, Robin Humphry-Baker, Ngoc-Le Cevey-Ha, Raphael Charvet, Pascal Comte, Shaik M. Zakeeruddin, and Michael Gratzel, J.Phys.Chem.B, Vol. 108, pp. 17553-17559 (2004)
- [Wan-2006] Qing Wang, Seigo Ito, Michael Gratzel, Francisco Fabregat-Santiago, Ivan Mora-Sero, Juan Bisquert, Takeru Bessho, and Hachiro Imai. J.Phys.Chem.B, Vol. 110, pp.25210-15221 (2006)
- [Way-1993] P.C. Wayner, Langmuir Vol. 9, p.294 (1993)
- [Whi-2002] G.M. Whitesides & B. Grzybowski, Science, Vol. 295, p. 2418 (2002)
- [Yin-1999] J.Y. Ying et al, Angew. Chem. Int. Ed., Vol.38, Iss.56 (1999)
- [Yol-1985] B.E. Yoldas, & P.W. Partlow, Thin Solid Films, Vol. 129, p. 1 (1985)

- [Yol-1985] B.E. Yoldas, & P.W. Partlow, Thin Solid Films, Vol. 129 (1985)
- [Yue-2004] ZENG Long-Yue, DAI Song-Yuan, WANG Kong-Jia, PAN Xu, SHI Cheng-Wu, GUO Li, Chin. Phys.Lett., Vol. 21, No. 9 p. 1835 (2004)
- [Zha-1998] H. Zhang and J. Banfield, Journal of Materials Chemistry Vol. 8, p.2073 (1998)
- [Zha-2000] H. Zhang and J. Banfield, J. Phys.Chem. B, Vol. 104, 3481 (2000)