

UNIVERSITY OF BAHRAIN

College of Science

Department of Physics



Photo-Degradation of Dyes Using Co-Doped Nanostructured TiO₂ Films

A Thesis Submitted in Partial Fulfillment of the Requirements for the Master
Degree in Applied Physics

Submitted by

Alia Mustafa Islam

20071828

Supervised by

Dr. Hacene Manaa Associate Professor

Co-Supervised by

Dr. Mohamed Bououdina Assistant Professor

University of Bahrain

Kingdom of Bahrain

May 2018



Thesis Discussion Committee Decision

Student Name: Alia Mustafa Islam	Student ID: 20071828
Department: Physics	College: Science
Program: Masters in Applied Physics	
Thesis Title: Photo-degradation of Dyes using Co-doped Nanostructured TiO ₂ Films	
Supervisor Name: Dr Hacene Manaa	Student GPA: Click here to enter text.

The Discussion Committee met on 24-May-18 In The Physics Department. Upon discussing the student whose details are stated above in public, the discussion committee recommends the following:

The student is awarded a grade A in the thesis subject.

- ☐ Without making any changes to the thesis.
- ☒ After making the modifications attached with this decision.

Discussion Committee Members Approval:

Name

Signature

1. Dr. Hacene Manaa

(Advisor)

Click here to enter text.

2. Dr. Aqql Dakhel

(Internal Examiner)

Click here to enter text.

3. Dr Fryad Henari

(External Examiner)

Click here to enter text.

Abstract

Wastewater from various industries, including factories, laboratories and food industries, represent serious problems to the environment. Contaminated water can be dangerous and toxic on human beings, microorganisms and aquatic life. The contaminated water may contain a variety of chemicals such as azo dyes, heavy metals and bacteria. The aim of our study consists on the preparation of new nanostructured materials with enhanced properties and high catalytic activity for the degradation of industrial dyes. This paper devoted of the fabrication of microreactor based on nanostructured co-doped Titanium dioxide (TiO_2) thin films for the degradation of Rhodamin B (RhB) dye produced from industry's in the Kingdom of Bahrain. This study Investigate the structure, morphology, topography, optical properties, and photocatalytic degradation of RhB using Pure TiO_2 , Nd-doped TiO_2 and Nd-M (Fe, Cu, Ag and Cd) co-doped TiO_2 thin films. This films, were prepared by sol-gel dip coating method. The analysis explicate the anatase phase of TiO_2 for all samples. Atomic Force Microscopy (AFM) technique shows the topography and morphology of films. Band gap energy calculated using two methods. First, from photoluminescence, the band gap established from 3.25 to 3.14 eV for Nd- TiO_2 and (Nd,Fe)- TiO_2 respectively. In addition, defects found using same method. Then, Uv-visible spectroscopy method showed energy gap between 3.34 for Nd- TiO_2 and (Nd,Cd)- TiO_2 to 3.23eV for (Nd,Ag)- TiO_2 . Photo-degradation efficiency under UV light of TiO_2 gives the maximum percent about 75%. This efficiency decreases with doping to 20% for (Nd-Fe) doped TiO_2 film.

Dedication

I dedicate this thesis to my parents who taught me to trust in Allah, believe in hard work. To all my family who have been a great source of support and encouraging me to believe in myself. This thesis also dedicated to Dr. Mohamed Bououdina, my guide during my University career.

Acknowledgement

I would like to thank Dr. Mohamed Bououdina who supported this project and guided me towards its achievement and encouraged me throughout its accomplishment. I greatly appreciate him supervision and his Interest to my research subject. I also thank Dr. Hacene Manaa for supervising and encouraging me to carry out this thesis and for giving me of his precious time. In addition, I would like to thank Dr. Tewfik Souier who supported this project and helped me to understand and learn AFM and PL devices in Sultan Qaboos University. I would like to thank Dr. Faycal Bensouici who make a great effort to help me in this project. Also, I would not forget Dr. Aqeel Dakhel who helped me using Uv-visible spectroscopy. I also thank Mrs. Basma Al-Najar who helped me doing measurements and drawing some sketches.

List of Contents

Subject	Page number
Defense Committee's Approval	A
Abstract	B
Dedication	C
Acknowledgements	D
Table of Contents	E
List of Tables	G
List of Figures	H
Chapter One	
Introduction to the Study	
1.1 Nanotechnology and TiO ₂ thin films	2
1.2 Problem Statement	3
1.3 Objectives	3
1.4 Justification Of The Problem	4
1.5 Glossary	6
Chapter Two	
Background and History	
2.1 Theoretical Framework	8
2.1.1 Structure of TiO ₂	8
2.1.2 Optical properties of TiO ₂ thin films	11
2.1.3 Photo-Degradation of Dyes using TiO ₂ thin films	13
2.2 Previous Studies	15

Chapter Tree	
Experimental Procedure	
3.1 Sol-Gel Dip Coating Method	29
3.2 Characterization	31
3.2.1 X-Ray Diffraction	31
3.2.2 Atomic Force Microscopy	34
3.2.3 Photoluminescence	37
3.2.4 UV-Visible Spectroscopy	39
3.3 Photo-Degradation	40
Chapter Four	
Result and Discussions	
4.1 Crystal Structure Analysis by Rietveld Method	43
4.2 Surface Topography using Atomic Force Microscopy	52
4.3 Photoluminescence	59
4.3.1 Fluorescence mechanisms in semiconductors:	59
4.3.2 Photoluminescence Results and discussion:	61
4.4 UV-Visible Absorption Spectroscopy	75
4.5 Photo-Degradation Measurements	81
Chapter Five	
Conclusion and Recommendations	
5.1 Conclusion	88
5.2 Research Study's Recommendations and Suggestions	89
References	90
Abstract Translated to Arabic	92

List of Tables

No.	Subject	Page number
1	Peaks positions obtained by PDXL program	44
2	Rietveld analysis of (Ns,M)-co-doped TiO ₂ thin films (M=Fe,Cu,Ag and Cd)	48
3	lattice parameters, Ionic radius and volume of the thin films	49
4	Roughness parameters of the TiO ₂ films obtained by AFM image processing	58
5	Band gap energy for Nd-M (Fe,Cu,Ag and Cd) co-doped TiO ₂ thin films	74
6	Band gap energy calculated from Uv-vis and PL methods	77
7	Comparing different parameters between literature and this study	79

List of Figures

No.	Figure	Page number
1	Graphical abstract of nanoscale TiO ₂ Applications	2
2	Chemical structure of Rhodamine B (basic violet 10)	6
3	Crystal structure of anatase, rutile and brookite phases	10
4	Optical transmittance of TiO ₂ films (a) before annealing and (b) after annealing	12
5	Schematic diagram of photocatalytic process initiated by photon acting on the semiconductor	13
6	(a) XRD patterns; (b) AFM surface analysis; (c) Optical transmittance T(λ) and reflectance R(λ) spectra; (d) Optical band gap; (e) Optical absorption spectra of MB solution; (f) Degradation of MB as a function of UV-light exposure time for 24h	17
7	(a) XRD patterns of the TiO ₂ electrodes with different Fe contents, (b) SEM image of Fe-doped TiO ₂ electrode (nFe:nTi= 1.0:100): $\times 100k$, (c) Catalytic degradation of RhB by Fe-doped TiO ₂ electrodes under visible light, (d) Catalytic degradation of MO by Fe-doped TiO ₂ electrodes under UV light	19
8	(a) XRD patterns of TiO ₂ and Cu-TiO ₂ films deposited onto glass substrate, (b) SEM images of Cu-TiO ₂ , (c) AFM images of Cu-TiO ₂ , (d) Optical transmittance T(λ) and reflectance R(λ) spectral; (e) Degradation of MB dye as a function of the UV-light exposure time	21
9	(a) XRD patterns of TiO ₂ and Ag-TiO ₂ films deposited on glass substrate; (b) SEM images of 2% Ag doped TiO ₂ at high magnification; (c) Optical gap of Ag-doped TiO ₂ ; (d) Degradation of RhB dye as a function of the UV-light exposure time	23
10	(a) The XRD pattern of the Cd3A-TiO ₂ and Cd5A-TiO ₂ ; (b) AFM image of TiO ₂ film; (c) Relation between band gap energy of the films and dyes photodegradation; (d)	25

	The influence of the dyes concentration on the photocatalytic activity of Cd _{0.1} A-TiO ₂ film	
11	(a) XRD patterns of samples sintered at 500°C “a-undoped, b-0.5, c-1.0%, d-2.5, e- 5.0% Nd doped TiO ₂ and f-Ag coated; (b) Diffuse Reflectance UV-visible spectra of samples sintered at 500°C; (c) Photoluminescence spectra of samples sintered at 500°C; (d) SEM of 1.0% Nd doped TiO ₂ ; (e) Photocatalytic degradation of MO using undoped, Nd doped and Ag coated TiO ₂ photocatalysts in UV light	27
12	(Nd,M) co doped TiO ₂ thin films preparation using sol-gel dip coating method	30
13	Dip coating system	30
14	“Rigaku-Ultima IV” X-ray diffractometer	31
15	(a) Bragg’s law, (b) Mechanism of x-ray diffraction, (c) X-Ray Diffractometer	32
16	Atomic Force Microscope	34
17	(a) Etched Crystal Silicon, (b) The nano-tip on the TiO ₂ thin film	34
18	Sample Preparation	36
19	MultiMode Base with Scanner Mounted on Support Ring	36
20	NanoScope – Soft Tapping in Air software	36
21	(a) Fluorescence Spectrometer, (b) Fixing the sample in the Fluorescence Spectrometer	38
22	Photoluminescence Proses	38
23	(a) UV–VIS–NIR Spectrophotometer, (b) Fixed sample with reference sample in the spectrophotometer	39
24	Homemade photo-reactor system	40
25	Degradation of dye after 4 h	41
26	Lambda EZ 210 UV–vis Spectrophotometer	41
27	X-Ray diffraction pattern of (Nd,M) co-doped TiO ₂ thin films	43

28	Phase identification of x-ray diffraction pattern of pure TiO ₂ thin film	45
29	X-ray diffraction patterns of (a) pure ; (b) Nd-doped; (c) (Nd,Fe); (d) (Nd,Cu); (e) (Nd,Ag); (f) (Nd,Cd) co-doped TiO ₂ thin films	46
30	Ionic radius vs. Crystallite size and Microstrain	49
31	Evolution of lattice volume as function of ionic radii of M for (Nd.M) co-doped TiO ₂ thin films	51
32	AFM 2D Images of Nd-M (Fe, Ag, Cu & Cd) doped TiO ₂	54
33	AFM 3D Images of Nd-M (Fe, Ag, Cu & Cd) doped TiO ₂	56
34	Relation between Roughness and Crystallite size	58
35	Energy levels in the direct and indirect gap materials	60
36	Photoluminescence spectra of Nd-M (Fe, Cu, Ag & Cd) doped TiO ₂ (a) range: 350 to 600 nm (b) range: 450 to 700 nm	61
37	PL spectra of Pure TiO ₂ thin film (a) range: 350 to 600 nm (b) range: 450 to 700 nm	62
38	Energy diagram for pure TiO ₂	63
39	PL spectra of (Nd) doped TiO ₂ thin film (a) range: 350 to 600 nm (b) range: 450 to 700 nm	64
40	Energy diagram for Nd-doped TiO ₂	65
41	PL spectra of (Nd,Fe) co- doped TiO ₂ thin film (a) range: 350 to 600 nm (b) range: 350 to 600	66
42	Energy diagram for (Nd,Fe) co-doped TiO ₂	67
43	PL spectra of (Nd,Cu) co-doped TiO ₂ thin film (a) range: 350 to 600 nm (b) range: 450 to 700 nm	68
44	Energy diagram for (Nd,Cu) co-doped TiO ₂	69
45	PL spectra of (Nd,Ag) co-doped TiO ₂ thin film (a) range: 350 to 600 nm (b) 450 to 700 nm	70
46	Energy diagram for (Nd,Ag) co-doped TiO ₂	71

47	PL spectra of (Nd,Cd) co-doped TiO ₂ thin film (a) range: 350 to 600 nm (b) range: 450 to 700	72
48	Energy diagram for (Nd,Cd) co-doped TiO ₂	73
49	Optical Transmittance T(λ) and Reflectance R(λ) Spectral of Nd-M (Fe, Cu, Ag & Cd) co-doped TiO ₂ thin films	75
50	Optical gap of Nd-M (Fe, Cu, Ag & Cd) co-doped TiO ₂ thin films.	76
51	Variation of energy bandgap E _g as function of crystallite size of Nd-M (Fe, Cu, Ag & Cd) co-doped TiO ₂ thin films	77
52	Correlation between crystallite size and energy bandgap from literature	80
53	Optical absorption spectra of the Rhodamin B dye measured after the photocatalysis process for different exposure times. (a) Pure TiO ₂ , (b) Nd-TiO ₂ (c) (Nd,Fe)-TiO ₂ (d) (Nd,Cu)-TiO ₂ (e) (Nd,Ag)-TiO ₂ (f) (Nd,Cd)-TiO ₂	82
54	Schematic representation of cross sections of TiO ₂ thin films doped (a) with low Ag NPs concentration and (b) with too high Ag NPs concentration	83
55	Degradation of Rhodamine B dye as function of the UV-light exposure time	84
56	Corresponding plots for reaction rate constant Nd-M (Fe, Cu, Ag & Cd) doped TiO ₂	85
57	Histogram of variation of K _{app} as a function of different doping thin films	85

Chapter 1

Introduction to the Study

- 1.1 Nanotechnology and TiO₂ thin films**
- 1.2 Problem Statement**
- 1.3 Objectives**
- 1.4 Justification Of The Problem**
- 1.5 Glossary**

Chapter 1

Introduction to the Study

1.1 Nanotechnology and TiO_2 thin films

TiO_2 has been studied extensively because of its interesting properties and their use in various applications such as photocatalysis, optical coating, gas and humidity sensors, and as transparent electronic and dielectric materials, etc.

At the nanoscale, TiO_2 offers new applications in optoelectronics, solar cells, self-cleaning of glass, photoinduced hydrophilic properties at surfaces (Mangrola and Joshi, 2017, Diamond et al., 2017).

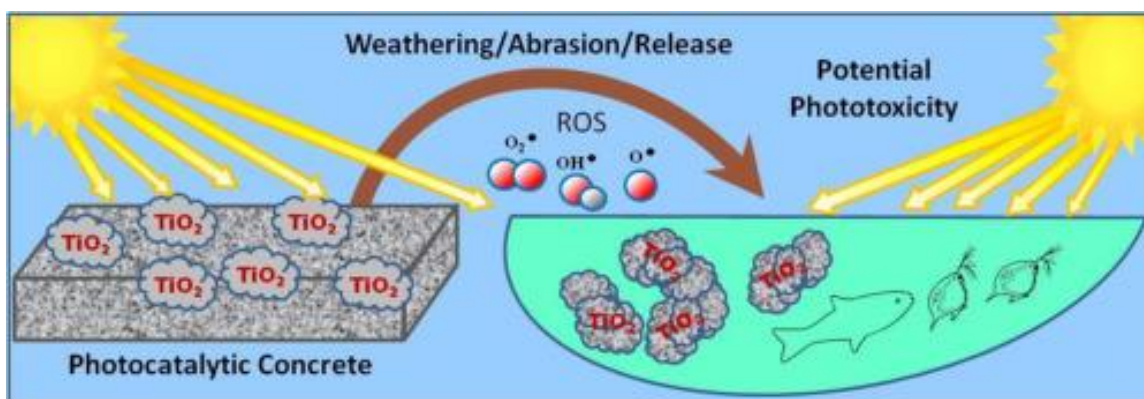


Figure 1

Graphical abstract of nanoscale TiO_2 Applications (Diamond et al., 2017)

Nowadays, numerous techniques are available for the deposition of TiO_2 thin films, including electron beam evaporation, sputtering, pulsed laser deposition, sol gel, spin coating, etc (Mangrola and Joshi, 2017).

1.2 Problem Statement

The aim of this research project is to investigate the efficiency of removal dyes from wastewater using co-doped TiO₂ thin films.

1.3 Objectives

The objectives of this project are:

1. The use of Nanotechnology to solve one of the most challenging worldwide problem, i.e. wastewater;
2. Develop new nanostructured materials with specific properties for the removal of dyes;
3. To characterize the developed nanostructured material by using some advanced techniques;
4. To carry out some measurements of removal dyes from contaminated water and end up with some conclusions;
5. To analyse and discuss of the obtained results.

1.4 Justification of The Problem

Wastewater from various industries, including factories, laboratories, and food industries, represents serious problems to the environment. Contaminated water could be dangerous and toxic on human beings, microorganisms and aquatic life (Akpan U.G. et al., 2009). The contaminated water may contain a variety of chemicals such as azo dyes, heavy metals and bacteria (Akpan U.G. et al., 2009).

Various physical methods and techniques have been proposed for the removal of dyes from contaminated water such as adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc (Ioannis, K. et al., 2004).

One of the most promising cost-effective and eco-friendly approach is photo-degradation of dyes using TiO_2 thin films. Photo-degradation and photo-catalysis consist of a series of reactions that are activated by absorption of a photon with sufficient energy (Akpan U.G. et al., 2009).

TiO_2 crystallizes into 3 phases: Anatase, Rutile, and Brookite. TiO_2 shows interesting properties, in particular being a semiconductor that can act as a sensitizer for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination and an empty conduction band (Akpan U.G. et al., 2009). From literature, Anatase phase was found to be the most attractive form of TiO_2 for photo-degradation of dyes (Akpan U.G. et al., 2009).

For this purpose, this research project will be devoted to the co-doping of TiO_2 thin film ($\text{Ti}_{0.96}\text{Nd}_{0.02}\text{M}_{0.02}\text{O}_2$) where $\text{M} = \text{Fe, Cu, Ag and Cd}$). Co-doping, a combination of a rare earth “Nd” (4f electrons) and a metal “Fe, Cu, Ag and Cd” (3d electrons) is expected to have a direct effect on phase

formation and stability (Anatase), microstructure (grain morphology and size, surface topography), optical properties (transmittance, reflectance, photoluminescence, and energy bandgap) and hence photo-degradation efficiency of RhB (as dye) as function of the nature of doping elements.

This research project is aimed to study the effect of co-doping nanostructured TiO_2 thin films, in terms of structure, morphology, and optical properties by using various experimental techniques including X-ray diffraction, atomic force microscopy as well as photoluminescence and Uv-visible spectroscopy. The photo-degradation of RhB dye was also examined.

1.5 Glossary

- 1- **Wastewater:** Any type of water that has been utilized in some capacity that negatively impacts the quality of the water such as water discharged from household, business and industries.
- 2- **Thin Films:** A microscopically thin layer of material that is deposited onto substrate (usually glass) with a typical thickness less than 500 nm, thin films could be conductive or dielectric.
- 3- **Doping:** The process of adding some impurity atoms in the **semiconductor**, known as dopants. Depending on the nature of the doping element and its concentration, the properties of the semiconductors can be tailored and tuned more effectively.
- 4- **Photo-degradation:** Chemical degradation of a material, any reduction or degradation in a useful property of a material because of a chemical change as a result of absorption of light.
- 5- **Rhodamine B (RhB)**

It is a chemical compound (dye) with a chemical formula: $C_{28}H_{31}ClN_2O_3$ (Bensouici, F. et al., 2015). It has various industrial applications such as tracer to determine rate/ direction of water flow and transport, biotechnology (because of its fluorescence), biomarker, analytical reagent, etc. Meanwhile, RhB has several effects on health/ environment including the cause of the mutagenic effect, toxic for fish, photo-allergic, and “may be” carcinogen for animals.

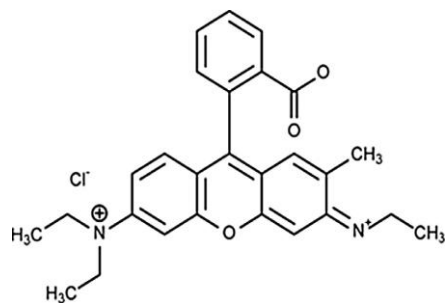


Figure 2
Chemical structure of Rhodamine B (basic violet 10)

Chapter 2

Background and History

2.1 Theoretical Framework

2.1.1 Structure of TiO₂

2.1.2 Optical properties of TiO₂ thin films

2.1.3 Photo-Degradation of Dyes using TiO₂ thin films

2.2 Previous Studies

Chapter 2

Background and History

2.1 Theoretical Framework

2.1.1 Structure of TiO₂

TiO₂ is among the top 50 materials being produced worldwide, because of its wide utilization as a main component of paints, pigments, glass products, biomedical implants, cosmetics, optical coatings, beam splitters and anti-reflection coatings because of its high dielectric constant and refractive index (Golubović et al., 2008).

The properties of TiO₂ nanoparticles are found to be change upon the type of crystal structure and its degree of crystallinity, particle morphology and size (also size distribution) as well as chemical composition (formation of point defects such as vacancies), thereby strongly dependent on the synthesis method (Reyes-Coronado et al., 2008).

TiO₂ crystallizes into three polymorphs: rutile (tetragonal, P4₂/mmn), anatase (tetragonal, I4₁/amd) and brookite (orthorhombic, Pbca) (Golubović et al., 2008) (Ennaceri et al., 2017). It is important to highlight that anatase phase is thermodynamically more stable compared to both rutile and brookite phases at particle sizes below 10 nm. On the other side, in the bulk form, rutile is thermodynamically most stable and thus annealing anatase at higher temperature than 500°C transforms into rutile (Kandiel, Ahmed and Bahnemann, 2016). Nevertheless, it is very challenge to synthesize thermally high stable anatase TiO₂ which can be either used as a

photocatalyst or as a support for metal nanoparticles for catalysis applications (Kandiel, Ahmed and Bahnemann, 2016).

Both anatase ($a = b = 3.78 \text{ \AA}$, $c = 9.50 \text{ \AA}$) and rutile ($a = b = 4.58 \text{ \AA}$, $c = 2.95 \text{ \AA}$) have tetragonal crystal structure, while brookite has an orthorhombic structure ($a = 5.43 \text{ \AA}$, $b = 9.16 \text{ \AA}$, $c = 5.13 \text{ \AA}$). It is important to highlight that the differences in crystal structures result in various densities and electronic structures of TiO_2 polymorphs (Etacheri et al., 2015).

Rutile TiO_2 is the most common form, which is hard and chemically resistant. The natural rutile contains 10% of Fe and traces of Nb and Ta. “Rutile” comes from the Latin word “*rutilus*” which means “red”, thereby it exhibits a deep red color and has many applications, including but not limited to: (i) a large amount of rutile in beach sands serves as an important component of heavy mineral sand ore deposits, which are eventually extracted to obtain rutile mineral for the production of refractory ceramic, Ti metal, and pigment; (ii) powdered rutile serves as white pigmentation for paints, paper, plastics, and foods; (iii) while nanoscale rutile particles are used for the effective absorption of ultraviolet rays, thereby mixed to produce sunscreens and to prevent skin damage. It is important to mention that Gems have greater value if rutile is among their constituents. Because it creates asterism (Differencebetween.net, 2017).

Anatase another polymorph of TiO_2 , transforms into rutile when annealed $\sim 915^\circ\text{C}$. Its color is brown to black or yellow to blue. Anatase is the rarest form, but has quite similar properties (hardness, density, and luster) as rutile. It offers various applications such as white pigmentation of paints, paper, and ceramics, but not advisable to be used outdoors because of its lower absorption rate compared to rutile (Differencebetween.net, 2017).

Brookite phase with an orthorhombic crystal lattice has a band gap energy equal to 3.4 eV. Moreover, both brookite and anatase irreversibly and exothermically convert to rutile at temperature above 600°C. Its activity has been rarely studied (Etacheri et al., 2015).

The experimental results reported in the literature reveal some important disagreement either in optical or electronic properties of brookite phase since it is not entirely crystalline (Díaz-Real, Ma and Alonso-Vante, 2016). Brookite has been proposed for several applications, such as DSSC cells.

The formation of anatase is dominated by surface energy effects, while the formation of rutile and brookite follows dissolution-precipitation mechanism, where chains of sixfold-coordinated Ti complexes arranged into different crystal structures. The synthesis of rutile results in relatively low surface area due to the formation of compact aggregates, while anatase and brookite consist of porous aggregates, and are suitable for applications in photocatalysis, sensors, and dye-sensitized solar cells (Reyes-Coronado et al., 2008)

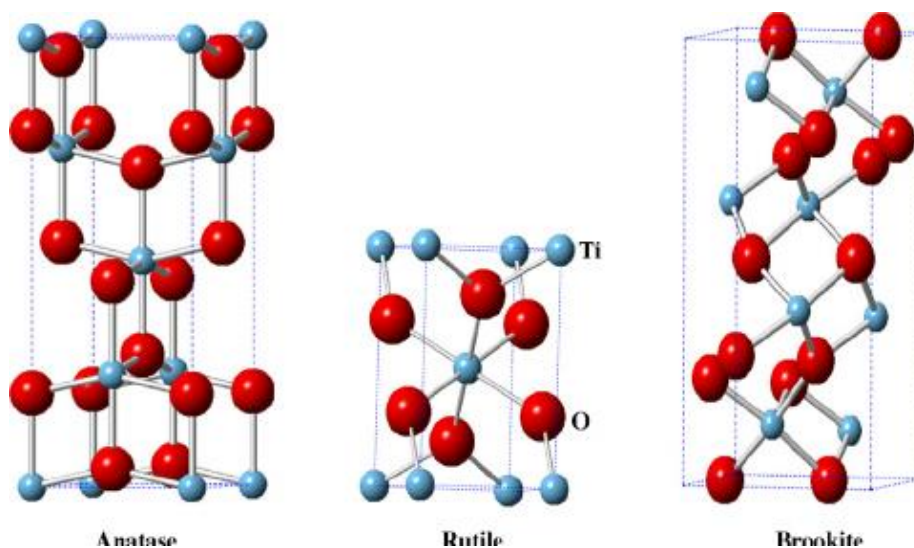


Figure 3

Crystal structure of anatase, rutile and brookite phases (Etacheri et al., 2015)

2.1.2 Optical properties of TiO₂ thin films

Compared to rutile and brookite phase, anatase TiO₂ has excellent photocatalytic activity, and shows long-term stability, lower cost and nontoxic.

With its wide band gap oxide semiconductor ($E_g=3.23$ eV), anatase only shows photocatalytic activity under UV-light irradiation ($\lambda<384$ nm), which represents only a small fraction ($\sim 5\%$) of the solar energy. The sun can provide an abundant source of photons, while the visible light accounts for a large fraction ($\sim 45\%$). Therefore, it is limited and very challenging to effectively utilize sunlight for extensive application of TiO₂. In this perspective, many attempts have been devoted to shift its absorption from UV-light to visible-light region, by doping TiO₂ with transition metal or nonmetal, noble metal loading, semiconductor compounding and organic dye sensitizing. Among these solutions, ions doping has been identified as a very simple procedure with low cost (Zongyan et al., 2015).

UV-Vis-NIR spectrophotometer is usually used to determine the optical transmittance and band gap energy. For example, it was found that the transmittance of TiO₂ decreases with increasing of substrate temperature during deposition (Figure 4-a). After annealing, the film becomes fully transparent in the visible and near-IR regions (Figure 4-b) (Miller and Wang, 2015).

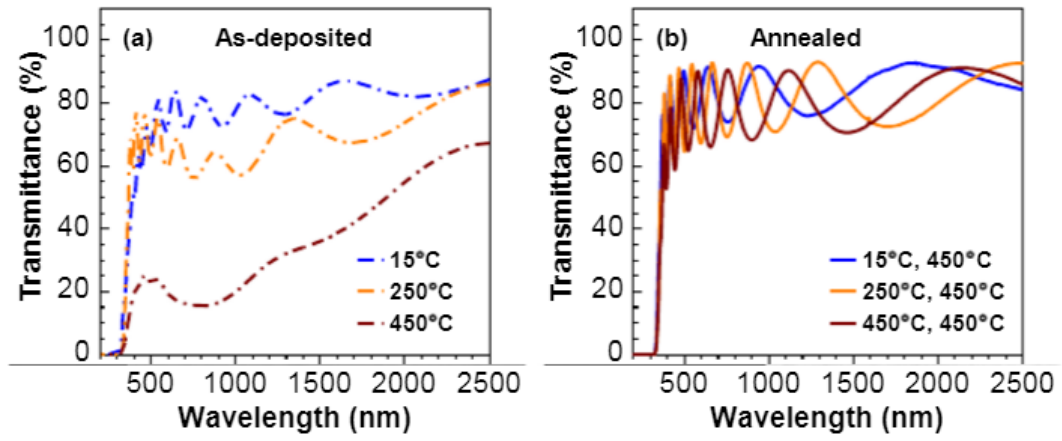


Figure 4
Optical transmittance of TiO₂ films (a) before annealing and (b) after annealing (Miller and Wang, 2015)

2.1.3 Photodegradation of dyes using TiO_2 thin films

The photodegradation process under UV–visible light source involves many stages: (i) the absorption of a photon by the photo-catalyst which causes charge separation; (ii) excitation of electron to conduction band of the catalyst resulting in the generation of active hydroxyl radicals by the oxidation of water molecules with photo-generated holes and oxygenated species that attack the dye molecules as shown in figure 5 (Khan S. et al., 2017).

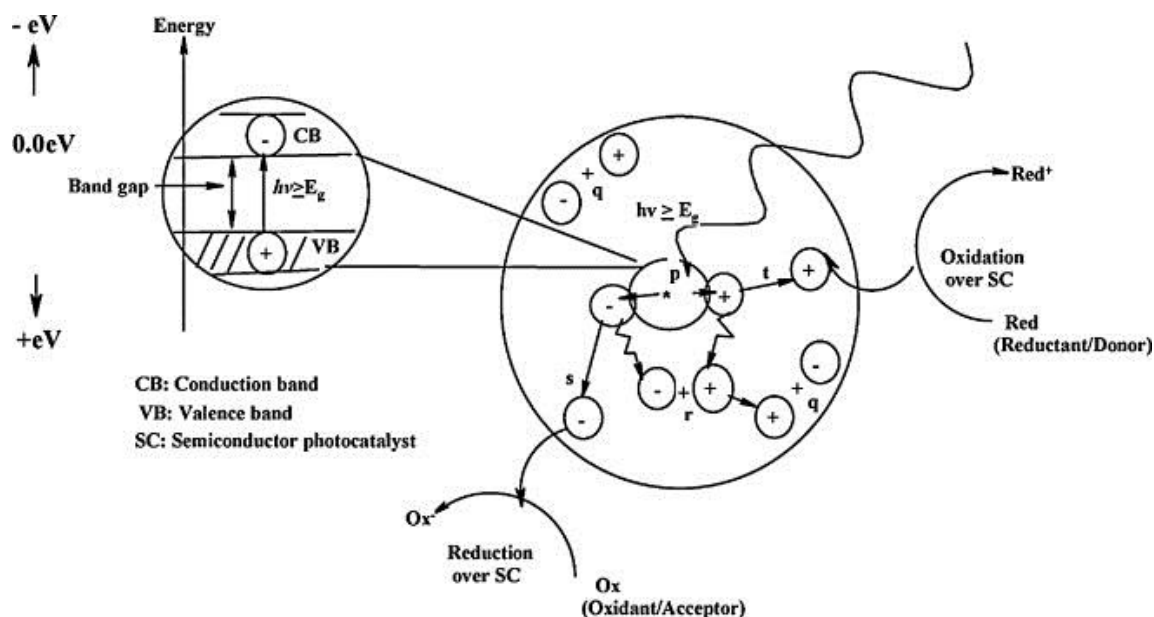
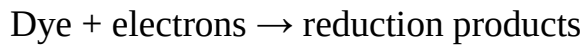
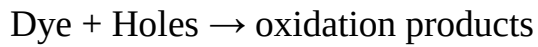
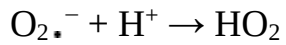
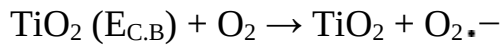
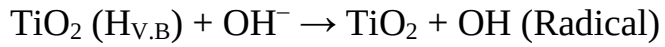
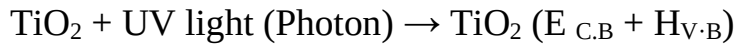


Figure 5

Schematic diagram of photocatalytic process initiated by photon acting on the semiconductor (Akpan U.G. et al., 2009)

The possible reactions involved in photodegradation are:



2.2 Previous Studies

Thin films based on TiO_2 with anatase phase have been extensively investigated as potential candidate for the photodegradation of dyes from wastewater. Many research papers have been devoted to the doping of TiO_2 using different elements, and deposition methods for better control of microstructure (particle morphology and size, surface topography) that has a direct influence on the evolution of optical properties (tuning of band gap) and thereby the photocatalytic activity.

TiO_2 thin films were prepared by dip-coating method. The prepared sols were obtained through the hydrolysis of tetraethyl-orthotitanate $\text{Ti}(\text{OC}_2\text{H}_5)_4$ under controlled pH by two different acids HNO_3 and HCl . From X-ray diffraction (Fig. 6a), only anatase phase is observed, with a slight preferred orientation along (004) reflection for $(\text{HNO}_3/\text{TiO}_2)$. Moreover, both lattice parameters and microstrain of $(\text{HNO}_3/\text{TiO}_2)$ are found to be higher than that of $(\text{HCl}/\text{TiO}_2)$. However, the crystallite size seems not to be influenced by changing the type of acid catalysis; ~ 16 nm. AFM surface analysis (Fig. 6b) reveals high density of nano-sized peaks forming an order network for $(\text{HNO}_3/\text{TiO}_2)$ while that of $(\text{HCl}/\text{TiO}_2)$ presents also peaks but are randomly distributed with the presence of a micro-size crack. Both surfaces are very smooth with an RMS below 4 nm, which should enhance their optical transparency. UV–VIS-NIR (Fig. 6c) shows the appearance of interferences indicating a good uniformity of the deposited films, meanwhile the energy bandgap (Fig. 6d) of $(\text{TiO}_2/\text{HCl})$ is slightly lower than that of $(\text{TiO}_2/\text{HNO}_3)$; 3.25 and 3.30 eV, respectively. A high degradation rate over 80% for $(\text{HNO}_3/\text{TiO}_2)$ is observed (Fig. 6e). It is also noticed that this efficiency remains stable even for films aged for 7 and 15 days (Fig. 6f), which shows

the stability of the solution prepared from HNO_3 . However, $(\text{HCl}/\text{TiO}_2)$ aged for 24 h shows a lower degradation activity ($\sim 40\%$), although XRD and optical measurements indicate the same crystallite size (16 nm) and optical bandgap (3.25 eV). Moreover, the efficiency of $(\text{TiO}_2/\text{HCl})$ thin films increases with the aging time; reaching a maximum value after 15 days and becoming similar to that of $(\text{TiO}_2/\text{HNO}_3)$; 80% (Bensouici et al., 2014).

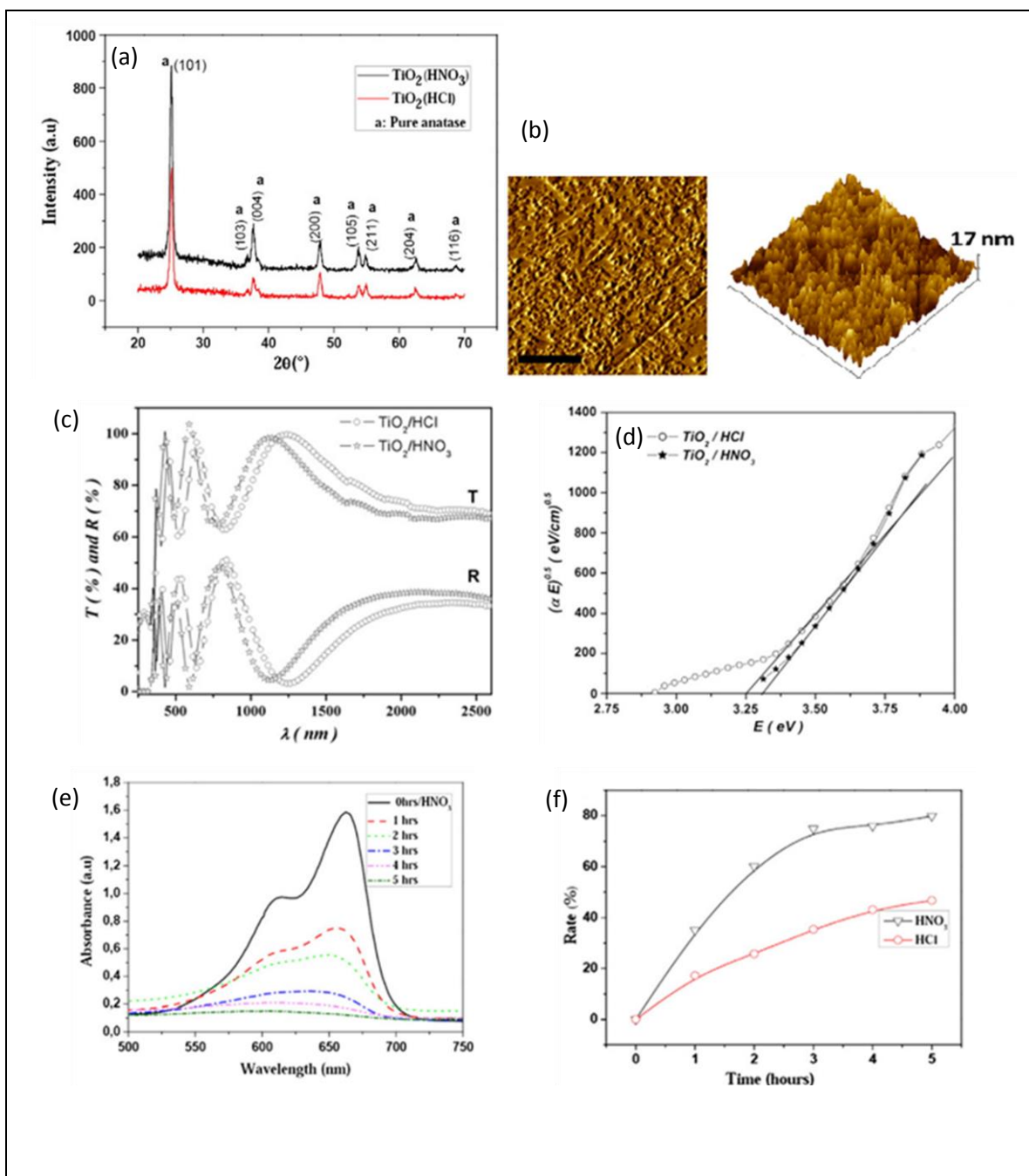


Figure 6

(a) XRD patterns; (b) AFM surface analysis; (c) Optical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra; (d) Optical band gap; (e) Optical absorption spectra of MB solution; (f) Degradation of MB as a function of UV-light exposure time for 24h (Bensouici et al., 2014).

Fe-doped TiO_2 was synthesized also using sol-gel dip-coating method due to its low cost and controllability. XRD analysis reveals anatase phase with small amount of rutile phase (Fig. 7a). With increasing Fe content, the grain size was found to increase slightly (17.9-22.6 nm) while the absorption spectra red shifted and energy bandgap decreased from 2.75 eV for TiO_2 up to 2.05 eV for 2% Fe. High magnification SEM observations (Fig. 7b) revealed nanoparticles having a close and uniform arrangement on Ti sheet with no cracks. Pure TiO_2 shows greater photocatalytic activity of MO (85%) under UV-light than Fe-doped TiO_2 , attributed to the mixture anatase/rutile phases (Fig. 7c), while the degradation efficiency decreases with increasing Fe doping. The decolorization rate of RhB (Fig. 7d) by the 1% Fe-doped TiO_2 film electrode was 22% higher than the undoped electrode under visible light (Tang, W. et al., 2014).

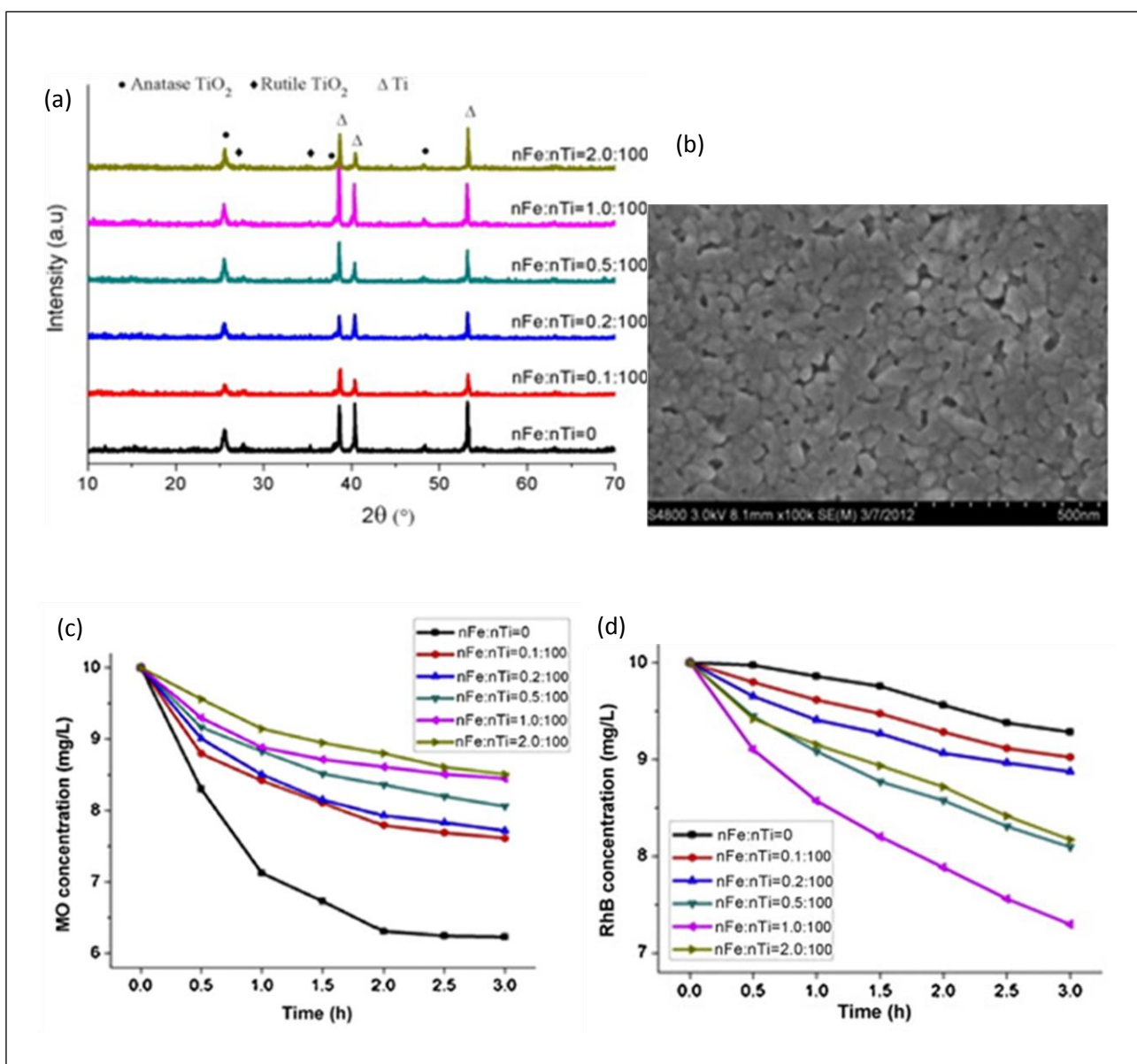


Figure 7

(a) XRD patterns of the TiO₂ electrodes with different Fe contents, (b) SEM image of Fe-doped TiO₂ electrode (nFe:nTi= 1.0:100): ×100k, (c) Catalytic degradation of RhB by Fe-doped TiO₂ electrodes under visible light, (d) Catalytic degradation of MO by Fe-doped TiO₂ electrodes under UV light (Tang, W. et al., 2014)

Similarly, Cu-doped TiO₂ films crystallized within anatase phase with a preferred orientation along [001] plane (Fig. 8a); the crystallite size did not very much influenced by Cu doping, i.e. around 17 nm. SEM observations (Fig. 8b) indicated granular nanostructure with grain size in the range 50–100 nm, but at higher magnification, each grain is in formed of fine particles with size less than 10 nm. The surface roughness (Fig. 8c) was found to increase with Cu content from RMS = 0.6 nm for low concentration (<0.4%) to RMS = 1.2–1.8 nm for intermediate concentration (2–6%). The UV-vis spectra (Fig. 8d) revealed very pronounced interference effects (good homogeneity of the deposited films' thickness) in the transparency region 300–2000 nm with sharp fall of transmittance at the band edge. The photocatalytic removal efficiency (Fig. 8e) of pure TiO₂ thin film reached about 92% of initial MB concentration after 180 min, then decreased drastically; only 16% for 4, 6 and 10% Cu-doped TiO₂ films (Bensouici, F. et al., 2017).

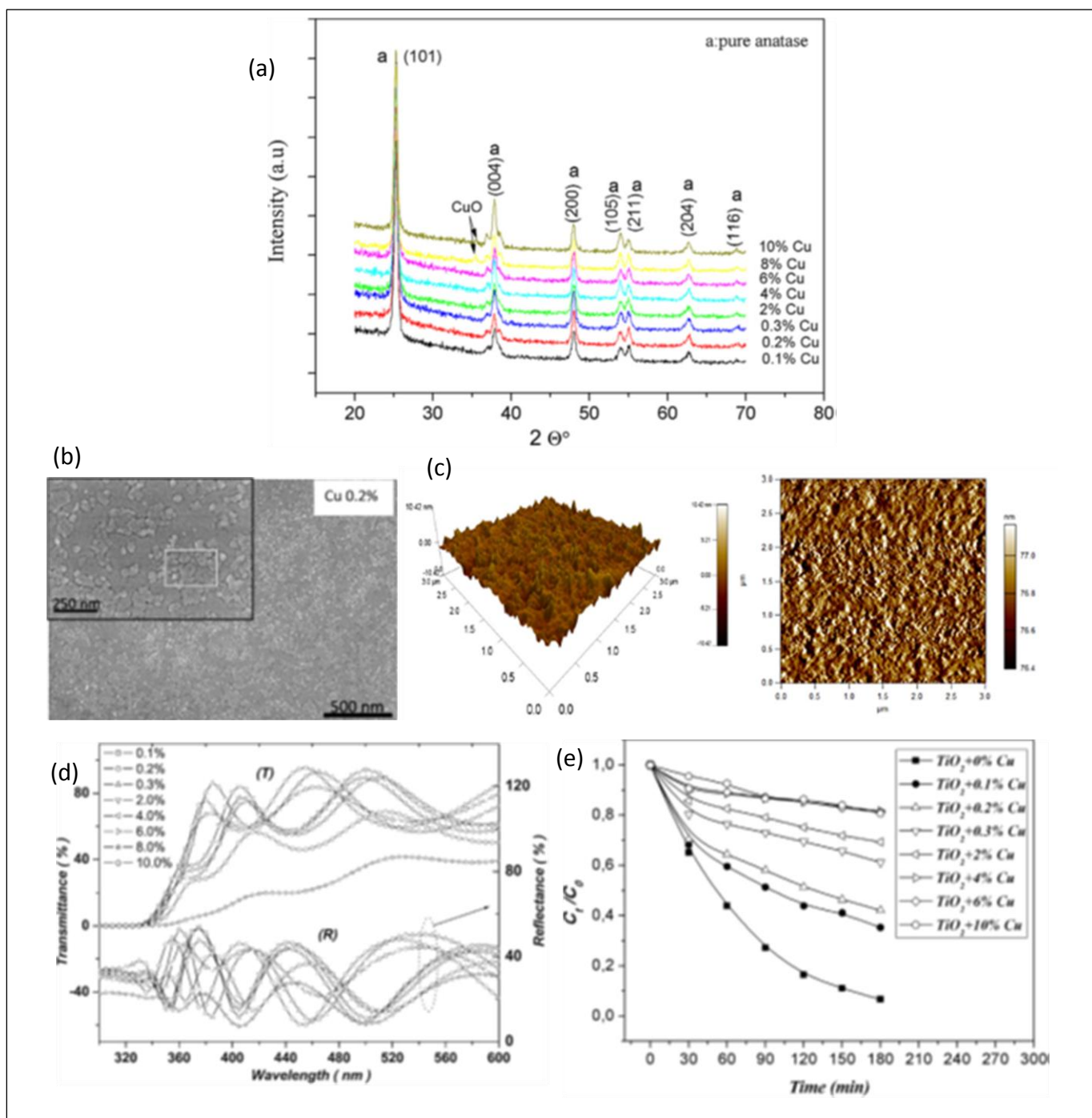


Figure 8

(a) XRD patterns of TiO₂ and Cu-TiO₂ films deposited onto glass substrate, (b) SEM images of Cu-TiO₂, (c) AFM images of Cu-TiO₂, (d) Optical transmittance T(λ) and reflectance R(λ) spectral; (e) Degradation of MB dye as a function of the UV-light exposure time (Bensouici, F. et al., 2017)

On the other hand, for Ag-doped TiO_2 , only anatase phase is observed (Fig. 9a). During the refinements, a preferred orientation along (004) reflection for TiO_2 was observed and the crystallite size remained around 17 nm. SEM observations (Fig. 9b) showed a high density of nano-craters (60-170 nm) with the presence of isolated nanoparticles (Ag-nano-dots 30 nm) having a tendency for aggregation (200 nm). Transmittance spectra (Fig. 9c) revealed very pronounced interference effect in the transparency region (300–2000 nm) with sharp fall at the band edge; whereas the energy bandgap varied slightly with Ag content, i.e. 3.09–3.31 eV. The photocatalytic removal efficiency (Fig. 9d) of TiO_2 doped by 0.5% Ag (mol) reached about 80% of initial RhB concentration after 5 h, while pure TiO_2 shows only 50% (Bensouici, F. et al., 2015).

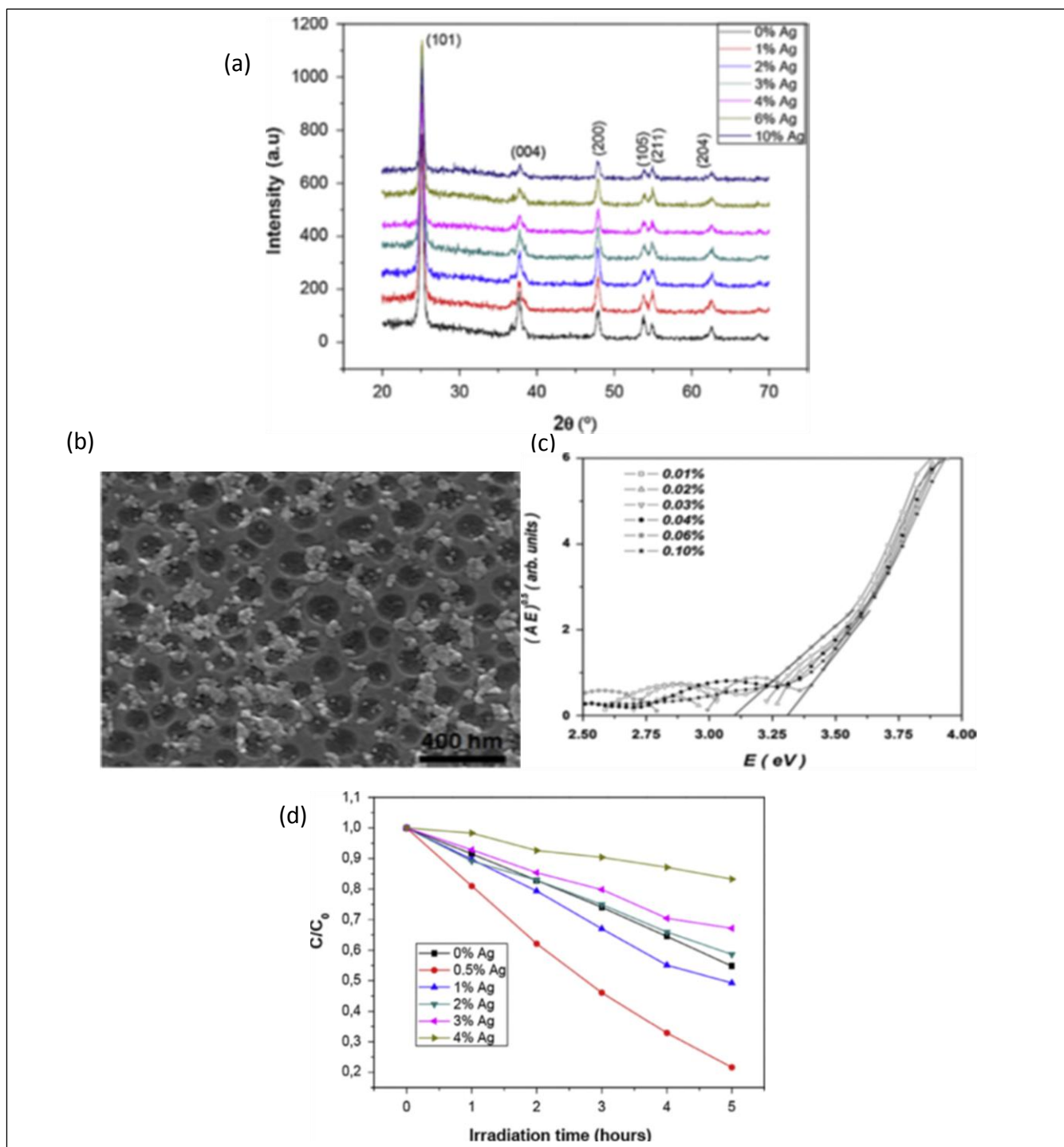


Figure 9

(a) XRD patterns of TiO₂ and Ag–TiO₂ films deposited on glass substrate; (b) SEM images of 2% Ag doped TiO₂ at high magnification; (c) Optical gap of Ag-doped TiO₂; (d) Degradation of RhB dye as a function of the UV-light exposure time (Bensouici, F. et al., 2015)

For TiO_2 doped with Cd (0.1, 0.5, 1 and 3%), both anatase and rutile phases were present (Fig. 10a). For higher Cd doping, a new phase CdTiO_3 appeared. AFM analysis (Fig. 10b) indicated that the films cover the entire area of the substrate surface with small grains having narrow size distribution, while the surface roughness increased the effective surface area. This resulted in an increase of the number of both active sites and defects. The transmittance spectra showed a shift of the adsorption edge (a blue shift for $\text{Cd}_{0.5}\text{A-TiO}_2$ and $\text{Cd}_{0.1}\text{C-TiO}_2$, red shift for remaining doped films) whereas the band gap decreased, see (Fig. 10c). Cd^{2+} doping is found to enhance the photocatalytic activity and can degrade methyl orange (MO) and MB with higher efficiency compared to un-doped TiO_2 ; 35 and 46% (Andronic, L. et al., 2009).

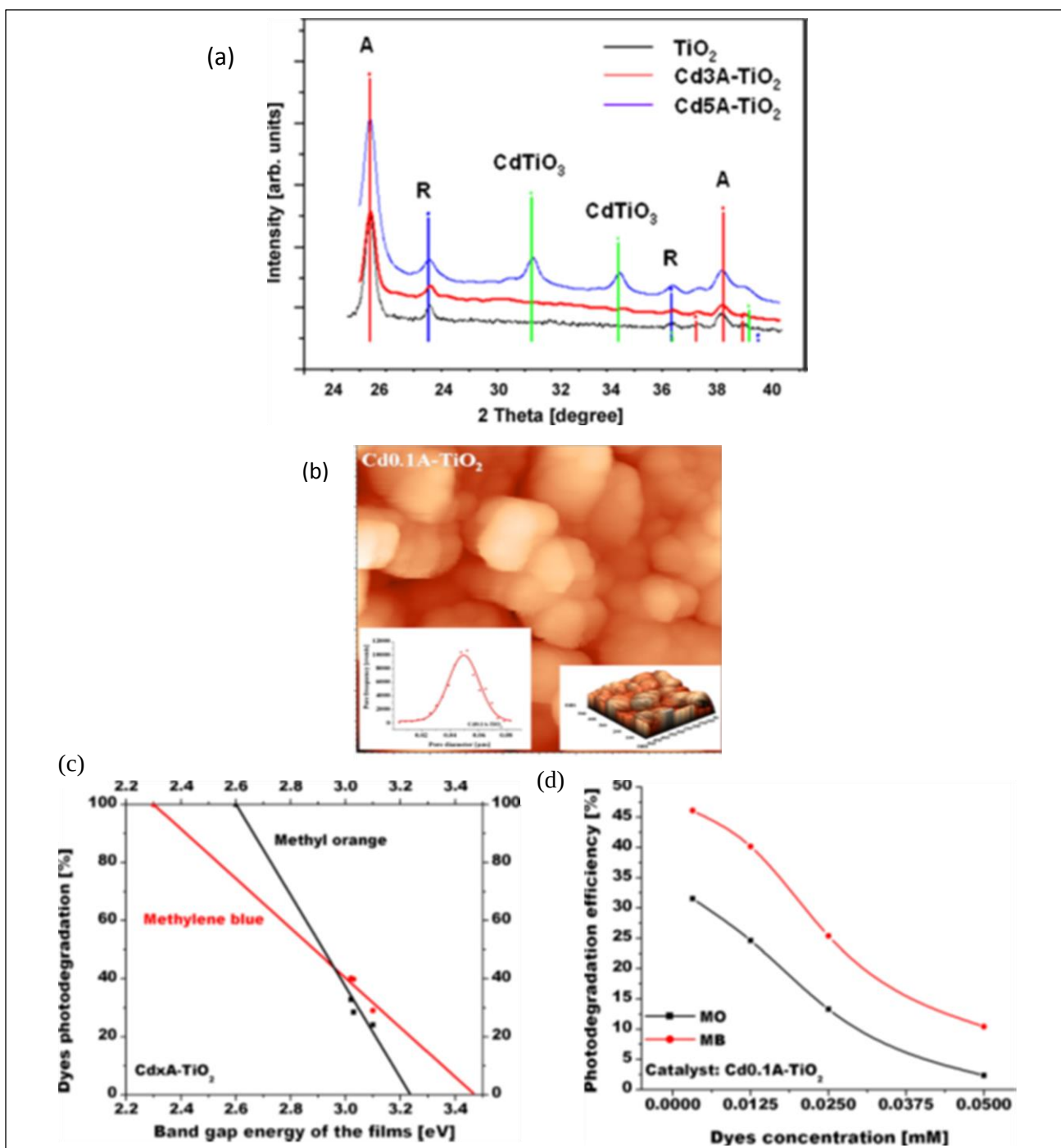


Figure 10

(a) The XRD pattern of the Cd3A-TiO_2 and Cd5A-TiO_2 ; (b) AFM image of TiO_2 film; (c) Relation between band gap energy of the films and dyes photodegradation; (d) The influence of the dyes concentration on the photocatalytic activity of Cd0.1A-TiO_2 film (Andronic, L. et al., 2009)

For rare-earth doping, it was found that Nd-doped TiO₂ films (Bokare, A. et al., 2013) crystallized within anatase phase with the presence of small amount of rutile phase (Fig. 11a), while the crystallite size decreased. UV-vis measurements (Fig. 11b) showed the presence of several optical absorption peaks with a slight red shift in their band gap transition as compared to un-doped TiO₂. Photoluminescence analysis (Fig. 11c) indicated the appearance of four main peaks: at 410 nm arising from self-trapped excitons near TiO₂ band edge (NBE); at 450 nm due to bound excitons; at 475 nm attributed to oxygen vacancies; and at 522 nm corresponding to the charge carriers formed after recombination. It is important to highlight that stronger the PL signal, higher the recombination rate of the photoinduced charge carriers as observed for undoped TiO₂. SEM images (Fig. 11d) of un-doped TiO₂ revealed particles with irregular in size and shape, whereas for Nd-doped films, the particles had uniform size and shape. The film with 1% Nd achieved the highest photocatalytic activity of 80% for the removal of MO dyes after 5h (Fig. 11e). The authors indicated that in addition, the suppression in the degree of recombination of electron–hole pairs with a decrease in band gap energy adds to the improved light absorbing capacity of the catalysts thereby favoring a higher degree of photocatalytic.

From this literature survey on pure as well as single doping TiO₂ films by transition metals (3d electrons) and rare earth elements (4f electrons), it is clear that single doped TiO₂ thin films show relatively low photocatalytic efficiency. Therefore, the proposed research project aims on the investigation of co-doped TiO₂ thin films; we propose fixed single rare earth doping (Nd: 2%) while varying the co-doping elements with fixed concentration (2%, M=Fe, Cu, Ag, and Cd).

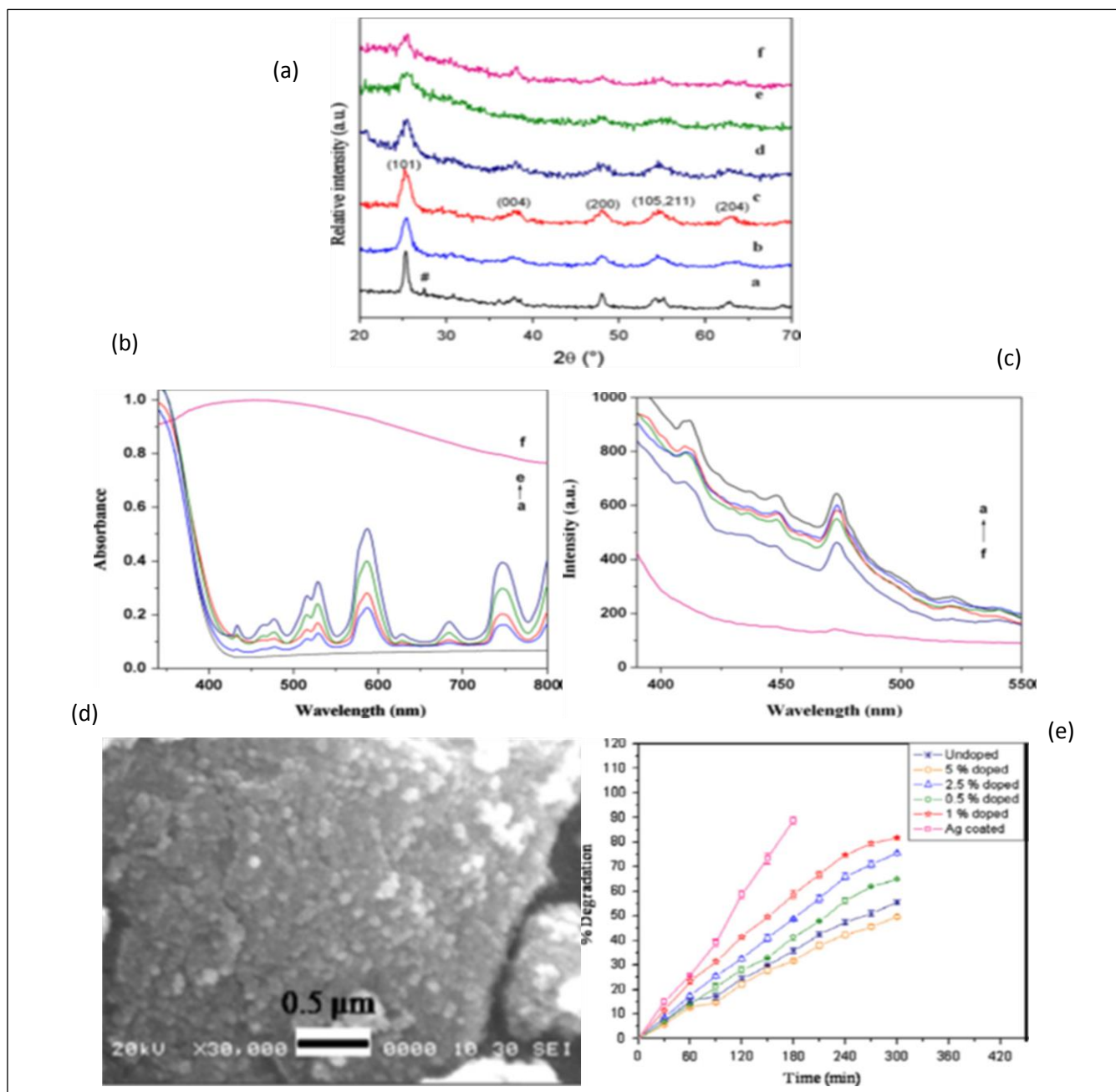


Figure 11

(a) XRD patterns of samples sintered at 500°C “a-undoped, b-0.5, c-1.0%, d-2.5, e-5.0% Nd doped TiO₂ and f-Ag coated; (b) Diffuse Reflectance UV-visible spectra of samples sintered at 500°C; (c) Photoluminescence spectra of samples sintered at 500°C; (d) SEM of 1.0% Nd doped TiO₂; (e) Photocatalytic degradation of MO using undoped, Nd doped and Ag coated TiO₂ photocatalysts in UV light (Bokare, A. et al., 2013)

Chapter 3

Experimental Procedure

3.1 Sol-Gel Dip Coating Method

3.2 Characterization

3.2.1 X-Ray Diffraction

3.2.2 Atomic Force Microscopy

3.2.3 Photoluminescence

3.2.4 UV-Visible Spectroscopy

3.3 Photo-Degradation

3.1 Sol-Gel Dip Coating Method

$\text{Nd}_{0.02}\text{Ti}_{0.98}\text{O}_2$ and $\text{M}_{0.02}\text{Nd}_{0.02}\text{Ti}_{0.96}\text{O}_2$ (M= Fe, Cu, Ag and Cd) thin films were deposited onto pre-cleaned glass substrates by a simple and cost-effective sol-gel dip-coating method. For un-doped TiO_2 , tetraethyl-orthotitanate (95% purity, Merk) precursor was dissolved in a solution containing ethanol, water and nitric acid as a catalyst in the solution (69% purity, Sigma-Aldrich), then stirred for 1 h. After aging for 24 h, the obtained gel was deposited onto glass substrate by a dip-coater using a withdrawal speed adjusted at 1 mm/s. The deposited layer thickness was controlled, indirectly, by the dipping number; in this case 2 dippings were applied giving an approximate thickness of 250 nm. For Nd- and M-doped TiO_2 , the sol gels were prepared following exactly the same procedure as described above, while $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99% purity, Biochem), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99% purity, Biochem), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99% purity, Biochem), $\text{Ag}(\text{NO}_3)$ (99% purity, Biochem), and CdCl_2 (99% purity, Biochem) were added to TiO_2 sol. This method is shown in figure 12 and 13. The as-prepared films were subjected to annealing in air Using Carbolite BLF 1800 at 450C for 1 hour.

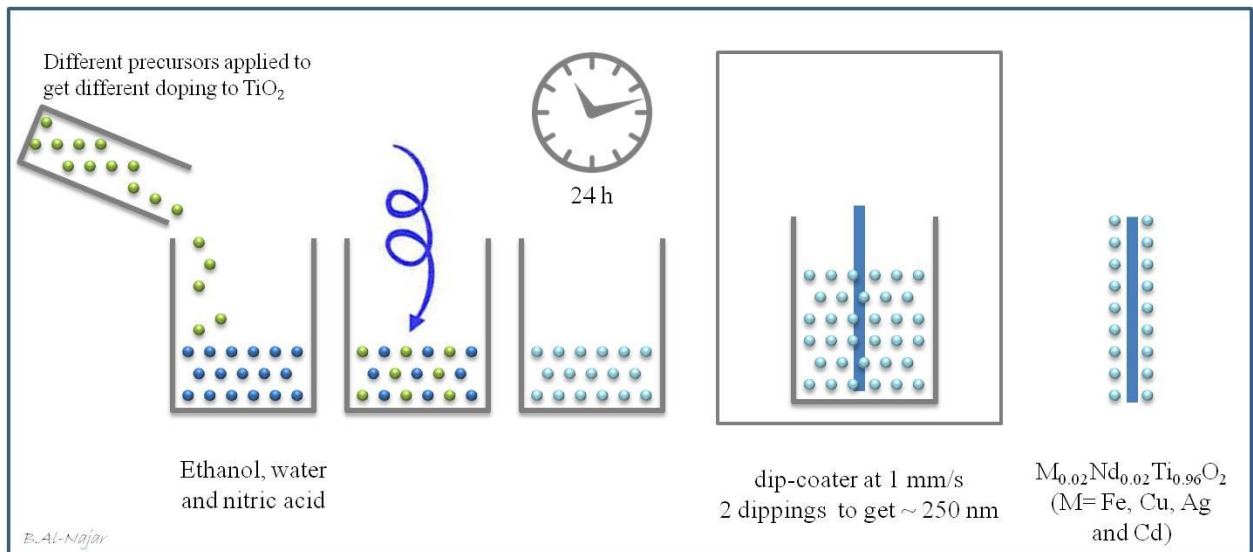


Figure 12

(Nd,M) co doped TiO_2 thin films preparation using sol-gel dip coating method

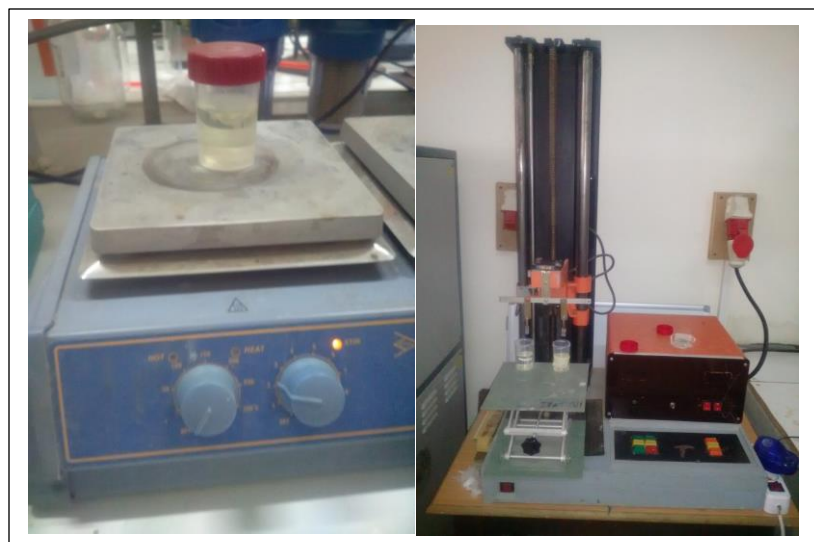


Figure 13

Dip coating system

3.2 Characterizations

3.2.1 X-Ray Diffraction

The structure of the prepared samples was characterized using X-ray diffractometer “Rigaku-Ultima IV”, as shown in Figure 14 (Rigaku.com, 2017).



Figure 14
“Rigaku-Ultima IV” X-ray diffractometer

In a theory of x-ray diffraction, the layers of a crystal act like weak reflecting mirrors for the X-rays. Only if the path difference of the reflected X-rays is a whole number of wavelengths does constructive interference occur, which is described by Bragg's Law (Fig. 15 (a) and (b)):

$$n\lambda = 2d\sin\theta \quad (1)$$

where λ is wavelength of the X-rays; d is the spacing of the layers; and θ is the incident angle of the photons.

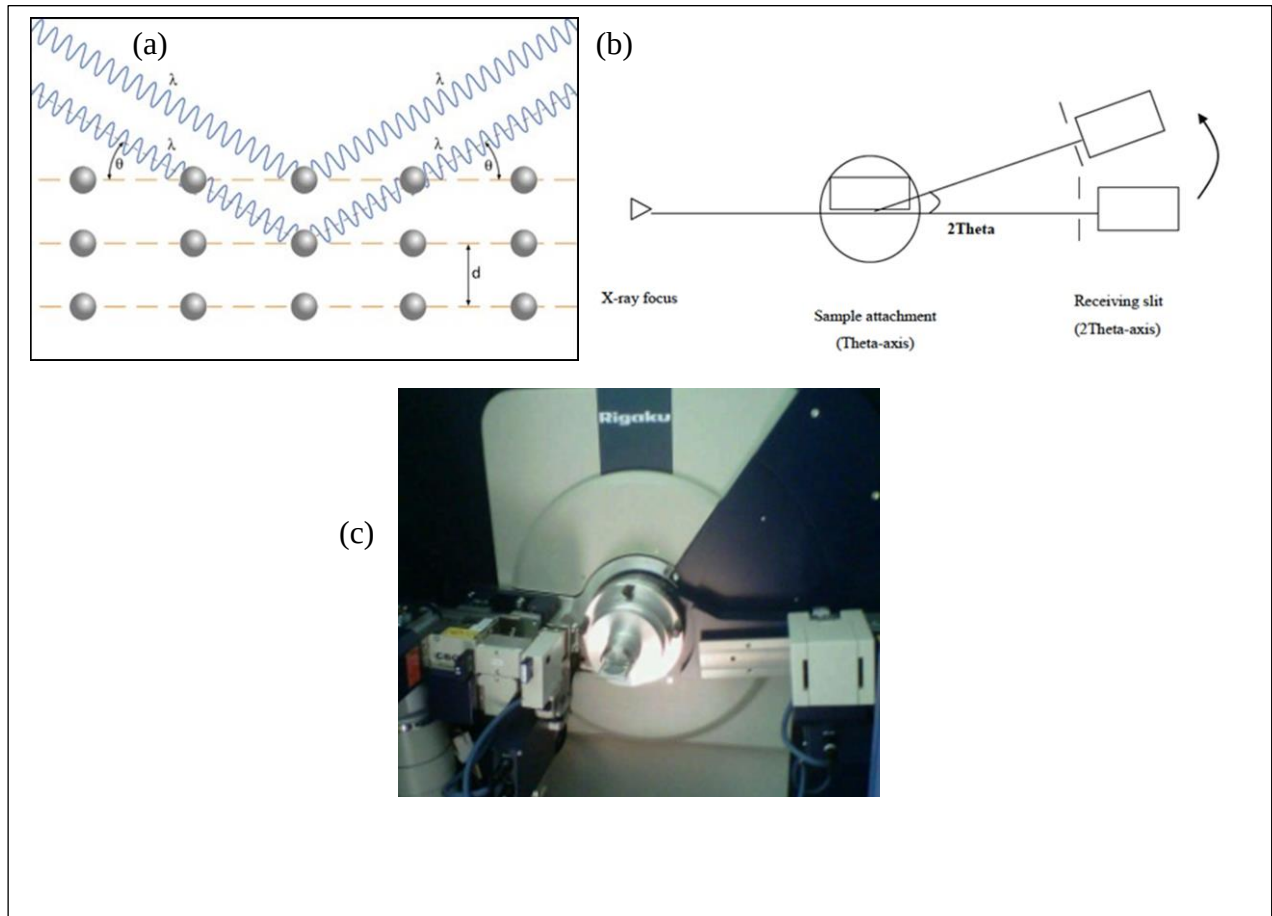


Figure 15

(a) Bragg's law, (b) Mechanism of x-ray diffraction, (c) X-Ray Diffractometer

The sample was fixed into the X-ray diffractometer (Fig. 15 (c)) and the experimental conditions were set:

Voltage : (40 V) ; Curent : (40 mA) ; Power : (1.6 kW)

2 θ -initial: 20°; 2 θ -final: 80°; step-angle: 0.04°; counting time: 1 second

The analysis of XRD patterns allow the following: phase formation, impurities, phase composition, determination of structural parameters (lattice parameters, atomic positions, occupancy, and thermal parameters) and microstructural parameters (crystallite size and microstrain), preferred orientation (grains for film and particles for powder), degree of crystallinity, etc.

Qualitative and quantitative phase analysis of X-ray diffraction patterns were performed by the Rietveld method using PDXL program supplied by Rigaku company. It is based on comparison between a theoretical based on the identified phases and experimental XRD patterns. The difference gives an indication about the quality of the refinements is assessed by using the following fitting criteria:

$$S = \frac{R_{wp}}{R_e}, \quad \chi^2 = S^2$$

where S^2 is the goodness-of-fit, R_{wp} is the weighted profile R-factor and R_e is expected T-factor.

Prior to that, phase identification is carried out using ICDD (International Centre for Diffraction Data) database, which will be for Rietveld refinements.

3.2.2 Atomic Force Microscopy

Atomic force microscopy (AFM) is a powerful tool for the evaluation of surface topography and roughness, morphology/ size of particles/ grains, etc. The Bruker represents the MultiMode scanning probe microscope (MM-SPM), it is designed for imaging small (approximately 15 mm diameter) samples using a series of interchangeable scanners (see Fig. 16).

In tapping mode, the contact forces can be minimized. An etched crystal Si tip cantilever probe oscillates near its resonant frequency. Because the cantilever is relatively stiff and oscillates at a high frequency, it possesses sufficient energy to break free of surface tension forces. This probe is more brittle and less forgiving than Si nitride, so precautions have to be taken into consideration (Fig. 17).

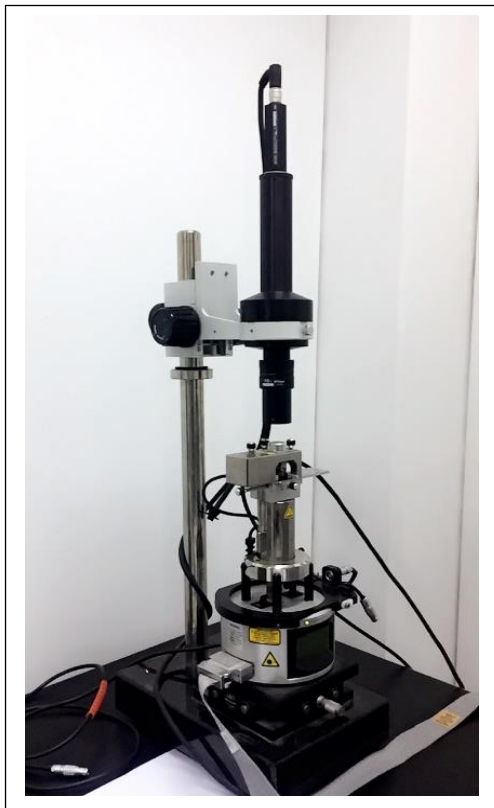


Figure 16
Atomic Force Microscope

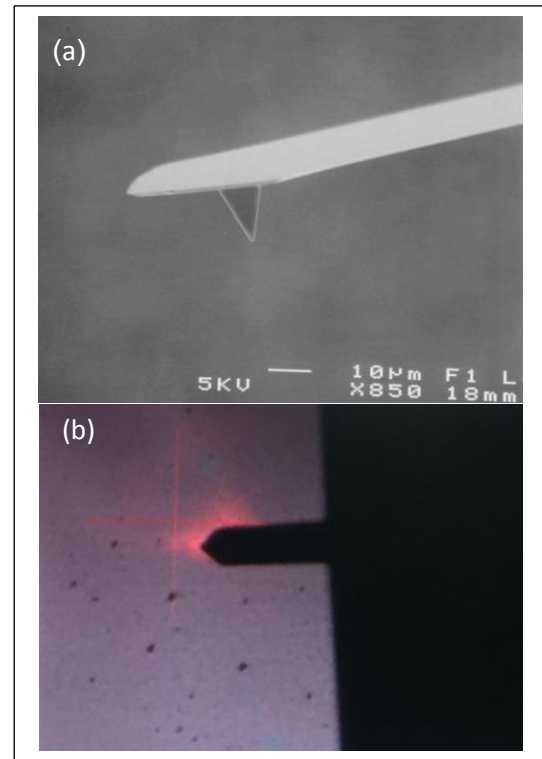


Figure 17
(a) Etched Crystal Silicon, (b) The nano-tip on the TiO₂ thin film

For preparing the sample, Firstly, verify that your sample will fit a top the scanner tube and is less than 8 mm thick. The calibration sample should be placed on metal disks of 15 mm diameter used for sample mounting. The MultiMode SPM is provided with several steel sample disks that can be attached to the magnetic sample holder, located atop the scanner tube. Then, Stick double-sided tape on the steel small sample puck, which will hold the sample to the disk. After that, Place the small sample to be imaged firmly on the tab as shown in Figure 18. Finally, Place the small sample disk atop the scanner (Fig. 19).

After preparing the sample, remove Head and Load Sample on the top of the scanner tube. An internal magnet holds the puck down.

After fixing the sample, NanoScope - Soft Tapping in Air software used to start scanning and take AFM images (Fig. 20). Then, WSxM4_0Beta8_4 software used to fix the images and draw 3D images. In addition, the last software used to find different parameters such as Kurtosis (R_{ku}), Skewness (R_{sk}) and Roughness (R_{ms} and R_a).

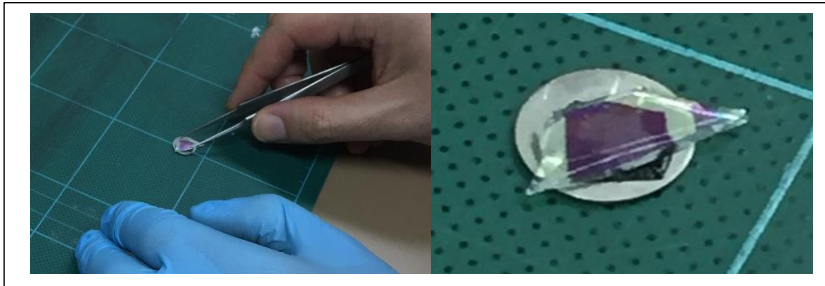


Figure 18
Sample Preparation

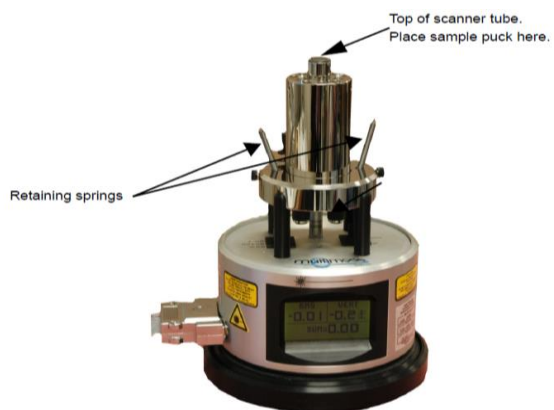


Figure 19
MultiMode Base with Scanner Mounted on Support Ring

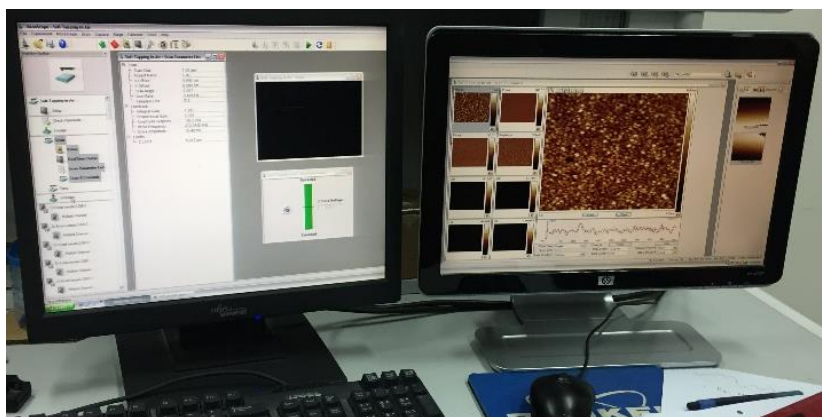


Figure 20
NanoScope – Soft Tapping in Air software

3.2.3 Photoluminescence

Photoluminescence (PL) is mainly used to determine the presence of points (vacancy, interstitial) defects. In addition, it can be used to estimate the energy band gap (E_g) using the equation (2):

$$E_g(eV) = \frac{hc}{\lambda(nm)} = \frac{1242.3}{\lambda(nm)} \quad (2)$$

where h is the Planck constant, c is the speed of light in vacuum and λ is the photon's wavelength.

Photoluminescence or Fluorescence starts with the absorption of a photon. Consequently, the absorption spectrum must be registered for any sample before starting with photoluminescence. This step will help to choose the ideal wavelength of excitation.

The fluorescence spectrometer used in this study is PerkinElmer LS55 (Fig. 21). The excitation wavelength is selected in such a way to get a maximum absorption by our samples. In our case, we chose the excitation wavelength to be 325 nm with energy higher than band gap energy ($E=3.82\text{eV} > E_g=3.2\text{eV}$).

As shown in the figure 22, the spectrometer consist of a broadband lamp that emits light in the ultraviolet region. Its radiation is dispersed and selected with the help of a monochromatic. The radiation is then focused on the sample with help of an appropriate lens. The sample's fluorescence is collected by another lens and send to another monochromator that is equipped with an optical multichannel analyzer for measurements. The electrical signal that is proportional to the optical signal is collected by a computer and analyzed with FL WinLab software. Another software called MagicPlotStudent was used for fitting the PL spectra with Gaussian curves.

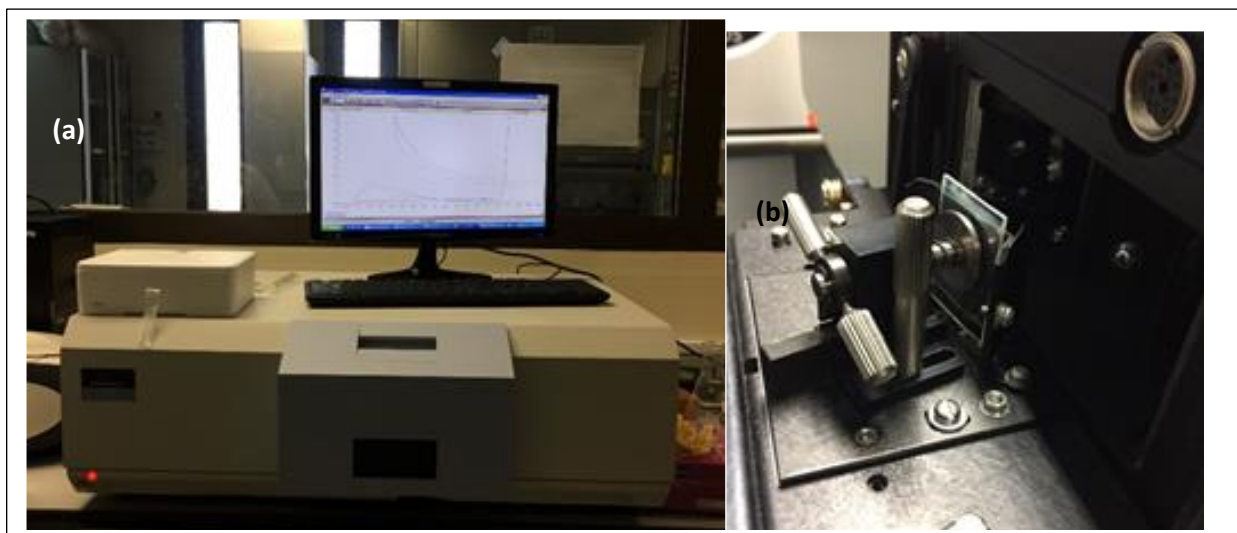


Figure 21

(a) Fluorescence Spectrometer, (b) Fixing the sample in the Fluorescence Spectrometer

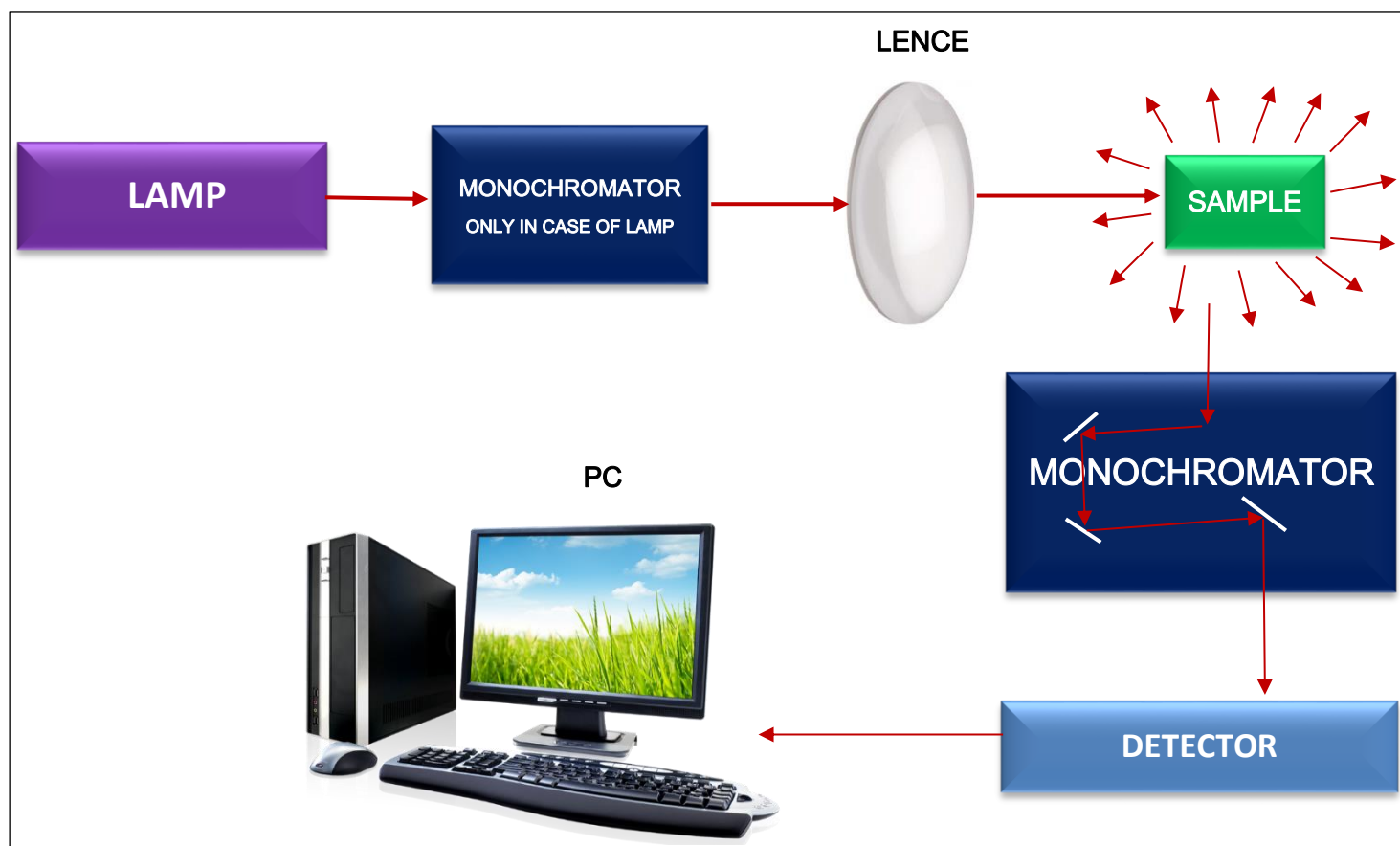


Figure 22

Photoluminescence Proses

3.2.4 UV-Visible Spectroscopy

Uv-vis spectroscopy is used to investigate the optical properties of the as-deposited nanostructured films. The spectral optical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were measured at normal incidence in UV–VIS–NIR spectral region 300–3000 nm (Fig. 23 (a)).

Two glasses are fixed into the spectrophotometer. As shown in figure 23 (b), the glass on the left is the sample which thin film is deposited on it, the one on the right is pure glass placed as a reference to subtract the noises.

UVProbe software used for getting data, which is supplied as standard with Shimadzu UV-VIS Spectrophotometers. Transmittance and Reflectance found separately using this software.

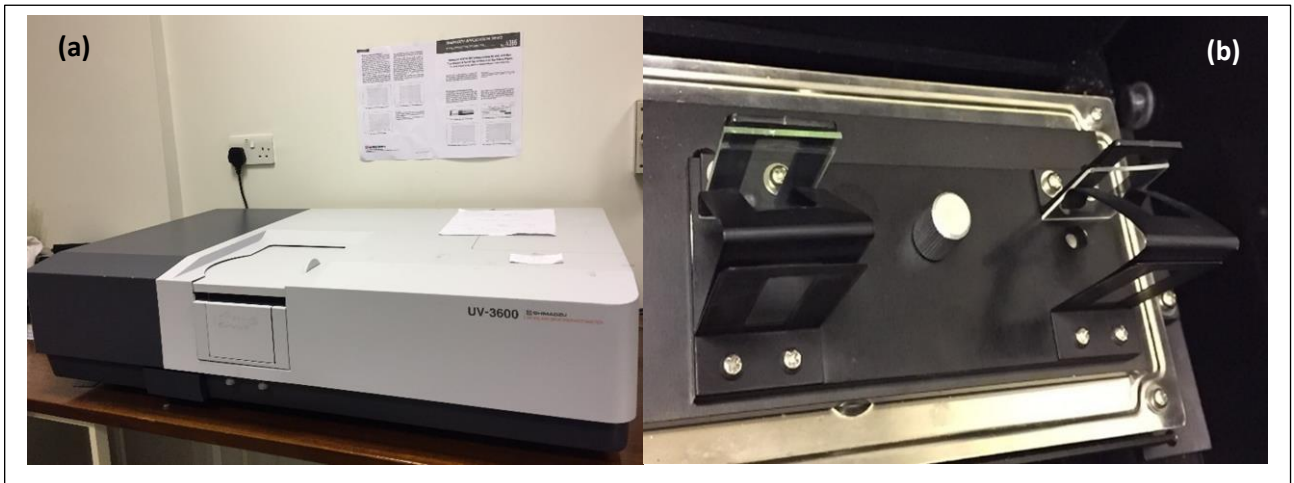


Figure 23

(a) UV–VIS–NIR Spectrophotometer, (b) Fixed sample with reference sample in the spectrophotometer

3.3 Photo-Degradation

Rhodamine B (RhB) with general formula ($C_{28}H_{31}ClN_2O_3$) and molecular weight $479.01 \text{ g mol}^{-1}$ (BIOCHEM Chemopharma) is highly water soluble and was usually used as a model solute.

The photocatalytic activity measurements were performed in a homemade system (Fig. 24). A 35 ml of RhB solution (at an initial concentration of $2.08 \times 10^{-5} \text{ mol/l}$) was introduced in a glass cell not transparent to UV light (capsule rounded bottom with a 45 mm diameter). The catalyst (thin film) was immersed into the cell containing the RhB solution (cell with solution and sample) at an angle of 70° to ensure that the surface is opposite to the radius of the UV lamp and the immersed surface is about $3 \times 2 \text{ cm}^2$. Then, the cells are exposed to UV-light at different exposure times (1, 2, 3, and 4 h) at room temperature. A 15W G15T8 Philips germicidal lamp was used as a UV source, emitting UVC light with a wavelength of 254 nm. The distance between the cell and UV lamp was 7 cm. Magnetic agitator used to homogeneous the pollutant solution on the surface of samples

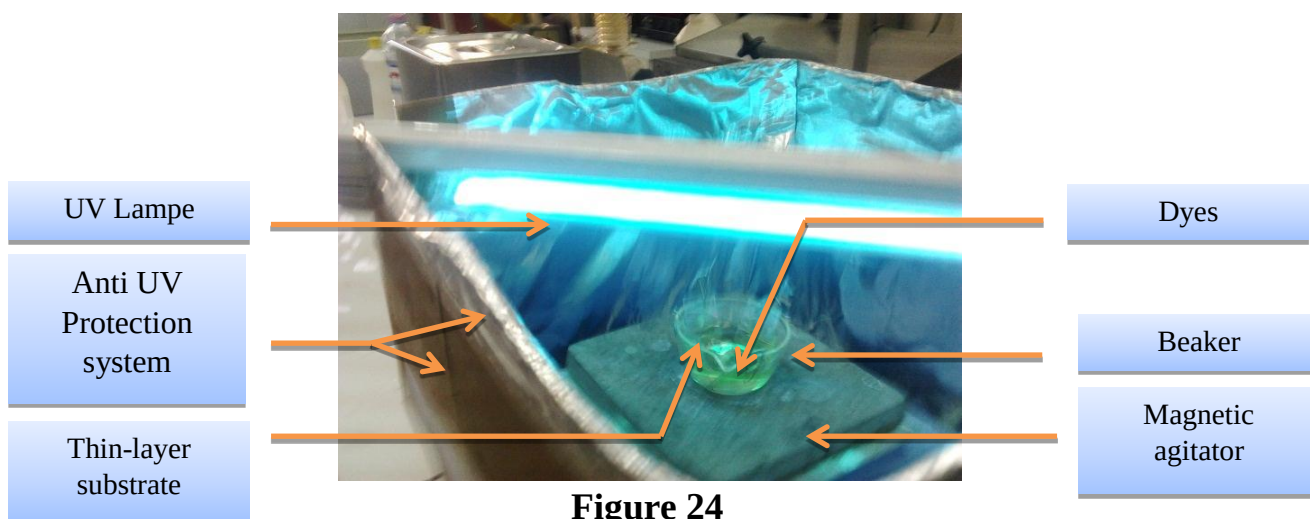


Figure 24

Homemade photo-reactor system

Degradation of
the Dye



Figure 25

Degradation of dye after 4 h



Figure 26

**Lambda EZ 210 UV-vis
Spectrophotometer**

Figure 25 shows the solution color after four hours when the dye is degraded. This RhB absorbance is measured with Lambda EZ 210 UV-vis spectrophotometer as shown in Figure 26.

Chapter 4

Result and Discussions

4.1 Crystal Structure Analysis by Rietveld Method

**4.2 Surface Topography using Atomic Force
Microscopy**

4.3 Photoluminescence

4.4 UV-Visible Absorption Spectroscopy

4.5 Photo-Degradation Measurements

4.1 Crystal Structure Analysis by Rietveld Method

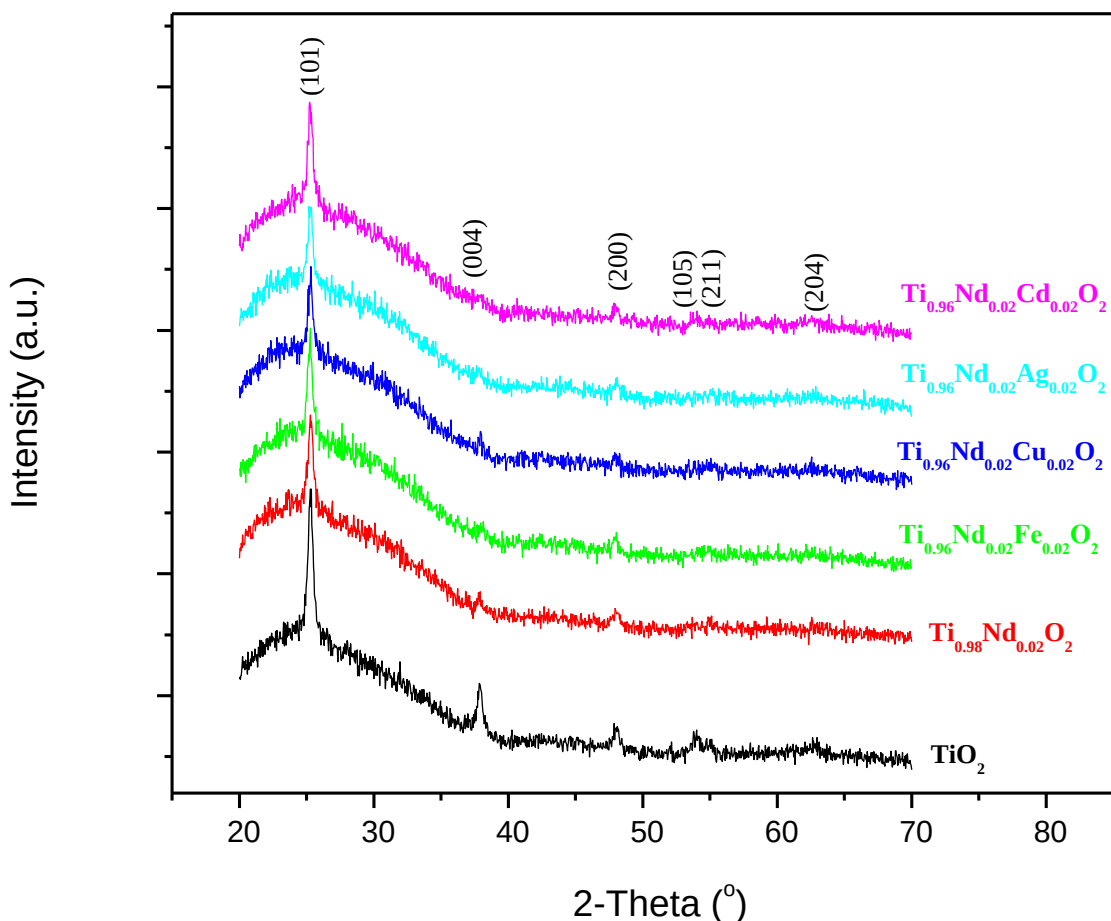


Figure 27

X-Ray diffraction pattern of (Nd,M) co-doped TiO₂ thin films

XRD patterns of pure, Nd-doped and M (Fe, Cu, Ag and Cd)-Nd co-doped TiO₂ films are shown in Fig. 27. All peaks are indexed within a tetragonal phase of anatase-type structure in agreement with JCPDS card No. 12-1272 (Fig. 28). Moreover, no additional diffraction peaks belonging to Nd and M species, or related compounds and oxides are observed, thus suggesting that both Nd and M metals are well dissolved into TiO₂ host lattice by occupying Ti sites. In addition, the formation of nano-dots (nano-clusters) that are well dispersed onto TiO₂ surfaces, and therefore cannot be

detected, i.e mixture, with X-ray diffractometer because of the small amounts of doping elements (Nd and M).

Figure 27 and table 1 indicates that the main peak is located around $2\theta=25.2797$. The halo in the range $2\theta=20-35$ can be attributed mainly to the amorphous glass substrate. In addition, it can be noticed from Figure 27 that the intensity decreases after doping while the peaks at higher angles almost disappeared.

Rietveld Analysis: Phase identification

Table 1
Peaks positions obtained by PDXL program

(hkl)	2θ (°)	Intensity
(101)	25.2797	100.0
(004)	37.5715	19.0
(200)	48.0265	24.2
(105)	53.6211	15.0
(211)	55.0389	14.6
(204)	62.5238	10.5

Rietveld analysis carried out on TiO_2 thin film shows a good fit (Figure 29), thereby confirming the formation of single anatase phase; both lattice parameters (a and c) and microstructural parameters (crystallite size and microstrain) were refined.

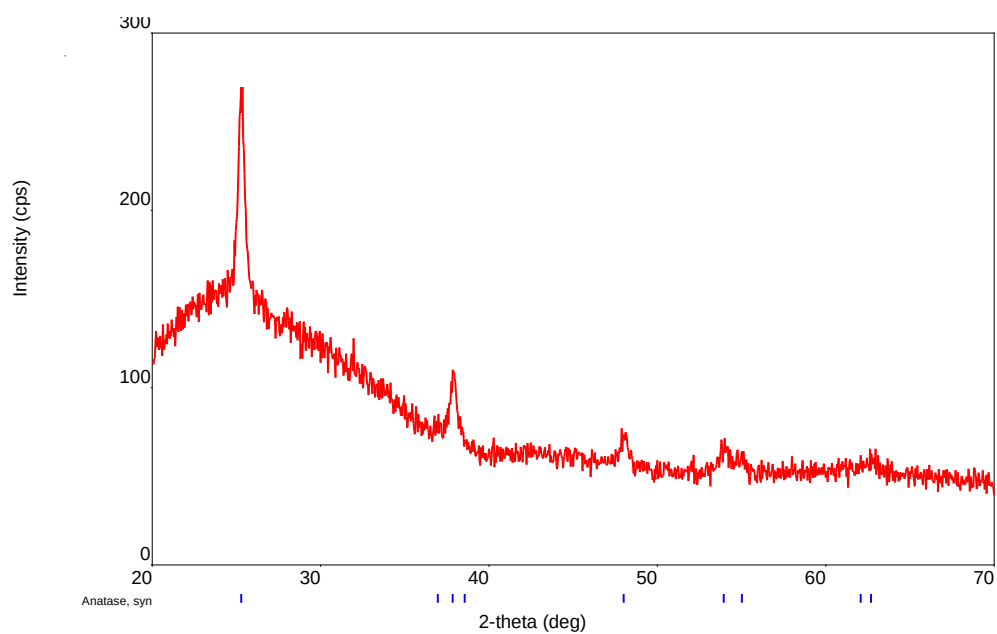


Figure 28
Phase identification of x-ray diffraction pattern of pure
 TiO_2 thin film

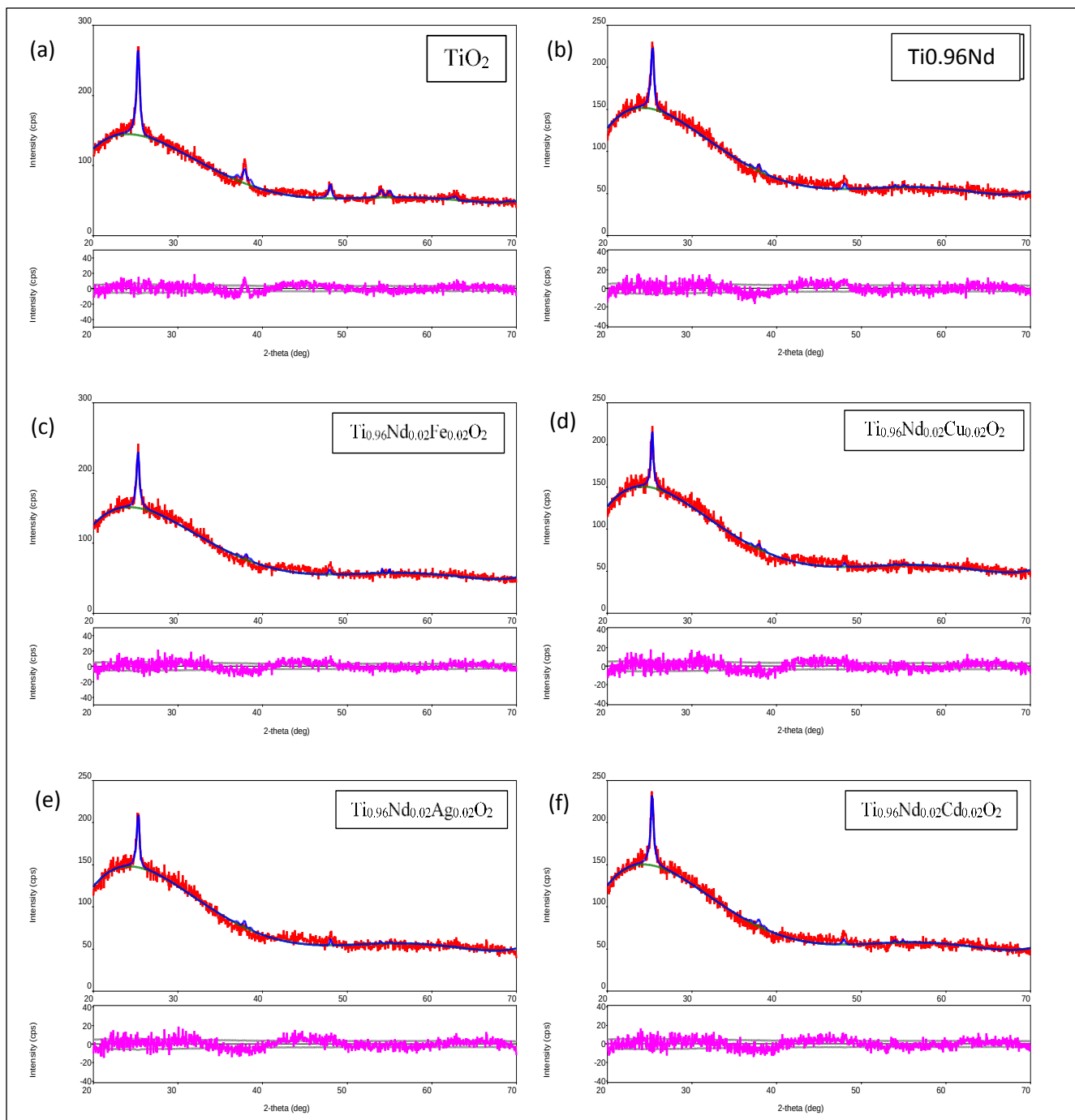


Figure 29

X-ray diffraction patterns of (a) pure ; (b) Nd-doped; (c) (Nd,Fe); (d) (Nd,Cu); (e) (Nd,Ag); (f) (Nd,Cd) co-doped TiO₂ thin films

XRD patterns refinements carried out using PDXL program confirm the formation of single TiO₂ phase as show in Figure 28, and the results of crystallite size, microstrain, lattice parameters are reported in Table 2. The fit parameters reported in Table 2 are in the range: Rwp = 6.31 – 6.62 %; Rp = 4.84 - 5.15%; Re = 4.88 – 4.94%; S = 1.29 – 1.35 and χ^2 = 1.67 – 1.82.

R_{wp} represents the weighted profile R-factor; Rp profile R-factor; Re is expected R-factor; S and χ^2 are goodness-of-fit parameters defined as follow:

$$S = \frac{R_{wp}}{R_e}$$

$$\chi^2 = \left(\frac{R_{wp}}{R_e} \right)^2$$

Table 2
Rietveld analysis of (Nd,M)-co-doped TiO₂ thin films (M=Fe, Cu, Ag and Cd)

Films	Crystallite size (nm)	Microstrain (%)	Lattice parameters (Å)	Fit Parameters				
				R _{wp} (%)	R _p (%)	R _e (%)	S	χ ²
TiO ₂	13.1 (2)	0.30 (3)	a= 3.789 (2) c= 9.493 (7)	6.61	5.16	4.93	1.3348	1.7914
Ti _{0.98} Nd _{0.02} O ₂	12.2 (3)	0.38 (6)	a= 3.787 (4) c= 9.492 (13)	6.31	4.84	4.89	1.2904	1.6650
Ti _{0.96} Nd _{0.02} Fe _{0.02} O ₂	13.3 (3)	0.35 (4)	a= 3.797 (3) c=9.461 (8)	6.52	5.08	4.88	1.3356	1.7839
Ti _{0.96} Nd _{0.02} Cu _{0.02} O ₂	15.0 (3)	0.32 (3)	a= 3.786 (4) c= 9.484 (18)	6.62	5.15	4.91	1.3483	1.8178
Ti _{0.96} Nd _{0.02} Ag _{0.02} O ₂	13.9 (4)	0.35 (4)	a= 3.785 (3) c= 9.499 (13)	6.55	4.99	4.94	1.3259	1.7580
Ti _{0.96} Nd _{0.02} Cd _{0.02} O ₂	12.6 (3)	0.36 (4)	a= 3.795 (3) c= 9.503 (12)	6.34	4.90	4.89	1.2956	1.6787

Phase composition Anatase 100%

Slight preferred orientation along (004) reflection for un-doped TiO₂ thin film.

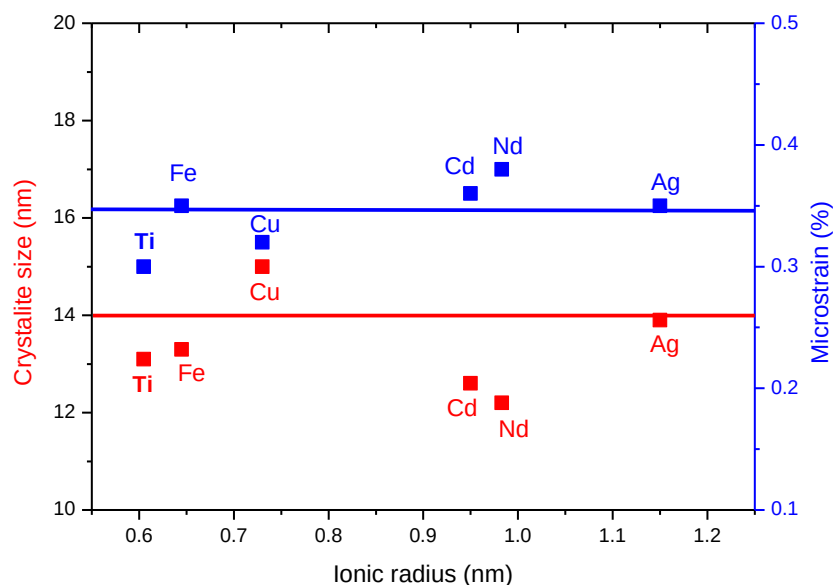


Figure 30

Ionic radius vs. Crystallite size and Microstrain

Using the table below, the volume of the unit cell was calculated using equation (3):

$$V = \frac{3\sqrt{3}}{2} a^2 \times c \quad (3) \quad , \text{ where } a \text{ and } c \text{ are lattice parameters.}$$

Table 3

Lattice parameters, Ionic radius and volume of the thin films

Films	a (Å)	c (Å)	Ionic Radius (Å)	V (Å³)
TiO₂	3.789	9.493	0.605	354.083
Ti_{0.98}Nd_{0.02}O₂	3.787	9.492	0.983	353.672
Ti_{0.96}Nd_{0.02}Fe_{0.02}O₂	3.797	9.461	0.645	354.381
Ti_{0.96}Nd_{0.02}Cu_{0.02}O₂	3.786	9.484	0.730	353.187
Ti_{0.96}Nd_{0.02}Ag_{0.02}O₂	3.785	9.499	1.150	353.559
Ti_{0.96}Nd_{0.02}Cd_{0.02}O₂	3.795	9.503	0.950	355.579

The effect of doping element on the evolution of microstructural parameters, for instance crystallite size and microstrain, is shown in Figure 30. It is clear, that no significant effect can be evidenced; i.e. with an average value of crystallite size around 14 nm and a mean microstrain value around 0.35%.

The variation of the unit cell lattice volume (Figure 31) shows a good correlation and can be divided into two main parts:

- Above the dashed line (upper part) indicates a dissolution of doping elements ($M = \text{Fe}^{3+}$ and Cd^{2+}) within TiO_2 host lattice resulting in an increase of the lattice volume (in agreement of ionic radii expansion) alongside with the creation of Ti^{4+} vacancies due to the unbalanced charges;
- Down the dashed line (lower part) indicates lesser dissolution of the doping elements ($M = \text{Cu}^{2+}$, Nd^{3+} and Ag^+) within TiO_2 host lattice due to a complex combination of several effects including a reduction of the lattice volume (even though their ionic radii are higher than that of Ti^{4+}), creation of O^{2-} vacancies due to the unbalanced charges as well as the formation of nano-clusters of metals that cannot be detected within the resolution of XRD measurements.

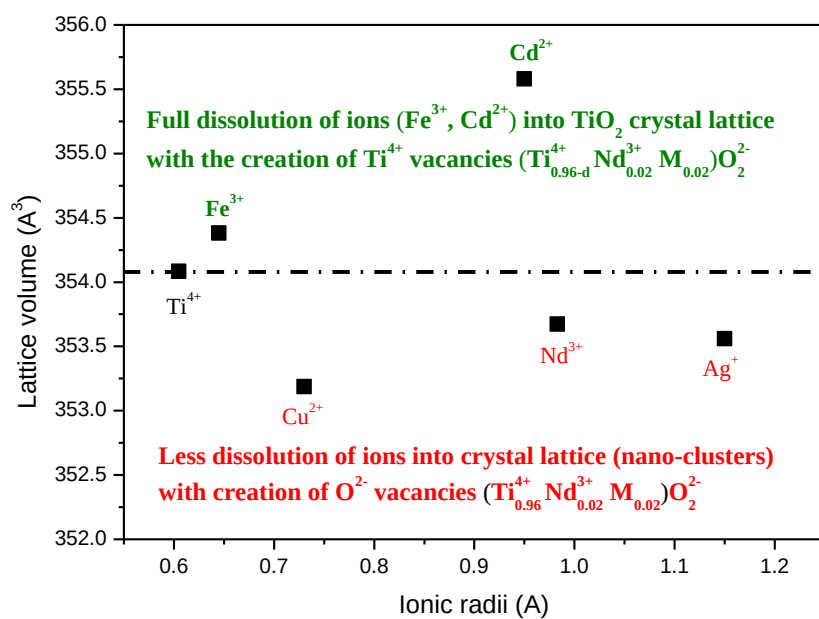


Figure 31

**Evolution of lattice volume as function of ionic radii of M
for (Nd.M) co-doped TiO₂ thin films**

4.2 Surface Topography using Atomic Force Microscopy

Amplitude modulation AFM imaging (Tapping mode) was used to characterize the surface morphology and roughness of the films. Topography scans of various M doped Nd-TiO₂ thin films are shown in Figs. 32 and 33. Statistical analysis was performed on all AFM images using Gwyddion software. Even though XRD did not show any peaks related to doping metals because of their small percentage, AFM images show important difference in terms of surface topography and roughness. Pure TiO₂ shows homogeneous arrangement of grains with typical size of 26 nm and maximum size of 40 nm (Fig. 32), while the 3D image shows sharp cones with a mean height of 4.8 nm (Fig. 32). The surface roughness was found almost constant (flat region) about RMS= 0.90 nm. Nd-doped TiO₂ thin film reveals almost similar behavior as pure TiO₂, having flat region with a roughness slightly higher RMS= 1.46 nm and while the height increases by double reaching about 9.1 nm. For co-doped TiO₂ thin films, important modifications in terms of topography and roughness are observed. Fe doped Nd-TiO₂ shows clear grains as pure TiO₂ with holes of sizes in the range 250-400 nm distributed throughout the entire film surface, at the same time the grain size increases drastically to around 70 nm while the roughness remains small of 1.23 nm and a height of 6.4 nm. On the other hand, Cu doped Nd-TiO₂ film surface shows same triangular-shaped cracks and holes with unclear particle with size of 20 nm, the highest roughness of RMS=5 nm and a height of 34 nm. Similarly, Ag doped Nd-TiO₂ thin film shows dark circular and triangular dots, which represent the holes of maximum size about 260 nm; the surface is smoother than Fe doped film with

grain size around 30 nm. The grains are not clear and the roughness is equal to 3.63 nm and a height of 29.3 nm. Finally, Cd doped Nd-TiO₂ is almost similar to Nd doped TiO₂ film but with larger height and lower surface roughness; the grain size is between 20 to 25nm with a roughness RMS=2.73 nm and height of 13.9 nm.

Figure 34 reveal, in general, a good correlation between the crystallite size estimated by XRD analysis and the surface roughness obtained by AFM analysis; smaller grains results in flat surfaces and lower porosity as “fine grains” can be compacted easily. In this regard, it is important to highlight that smooth surface is favorable for light harvesting while higher roughness results in light scattering but favorable for photocatalysis due to the presence of more active sites onto the surface (Haider et al. 2017).

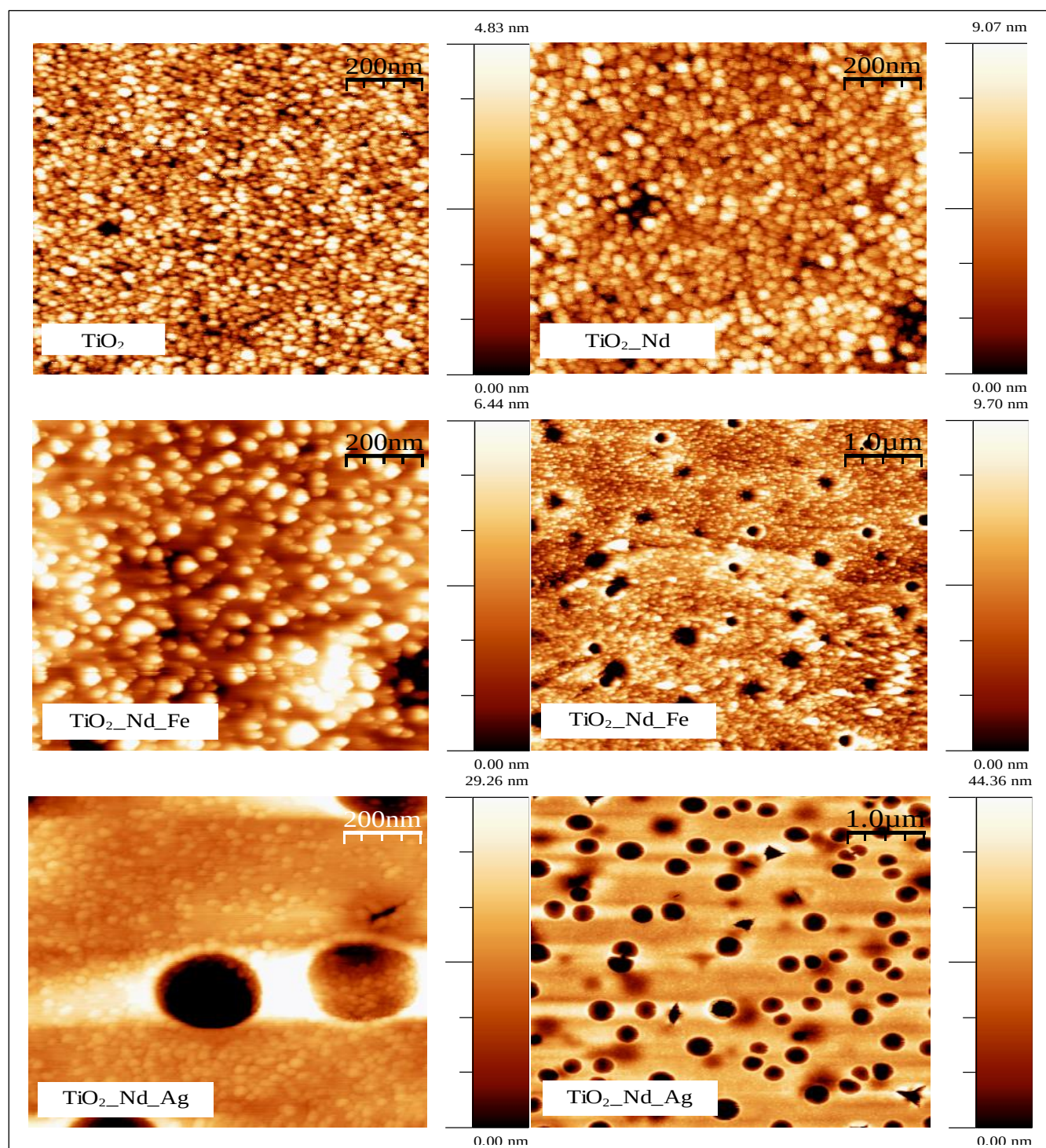


Figure 32

AFM 2D Images of Nd-M (Fe, Ag, Cu & Cd) doped TiO_2

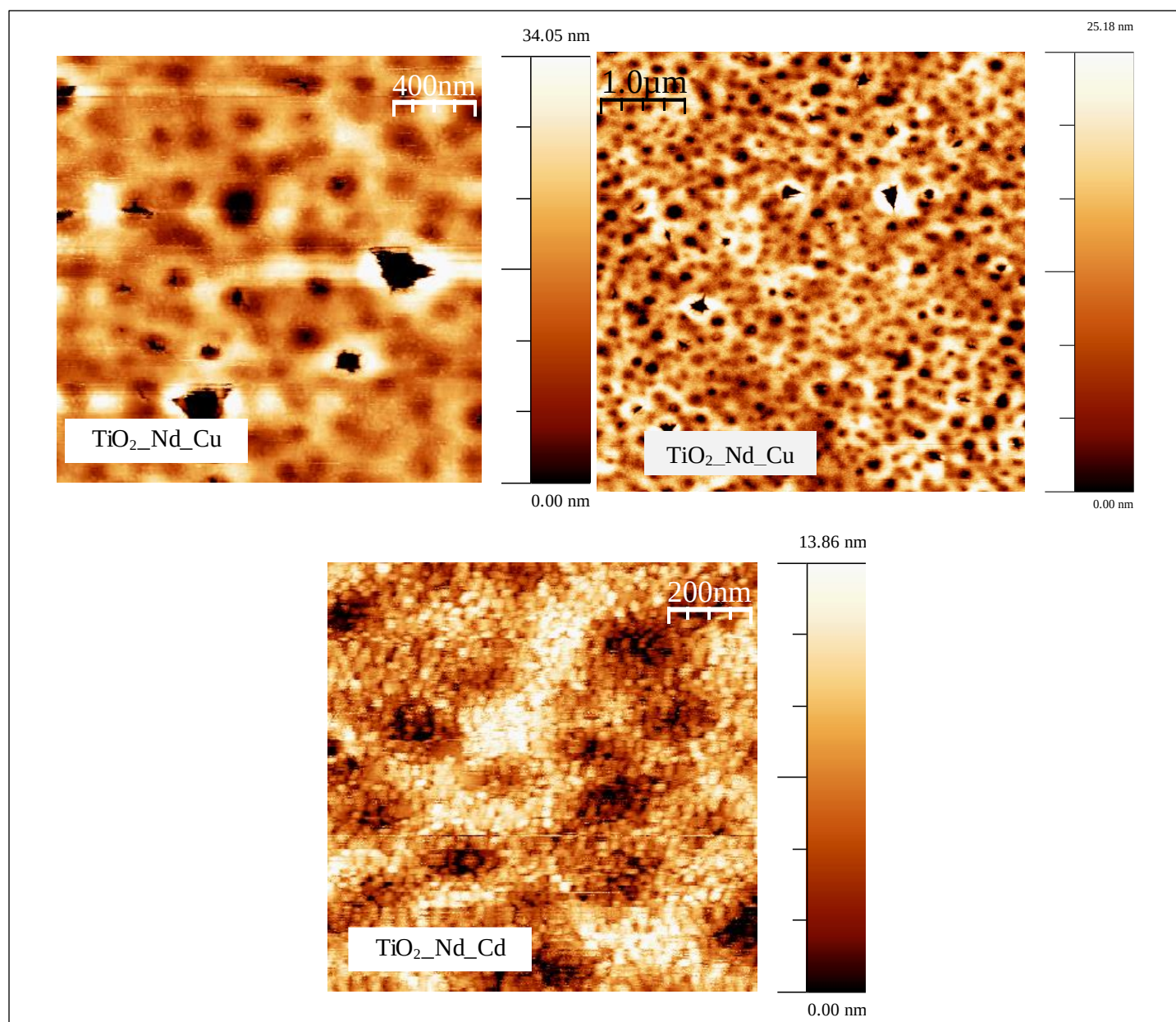


Figure 32 (continued)

AFM 2D Images of Nd-M (Fe, Ag, Cu & Cd) doped TiO₂

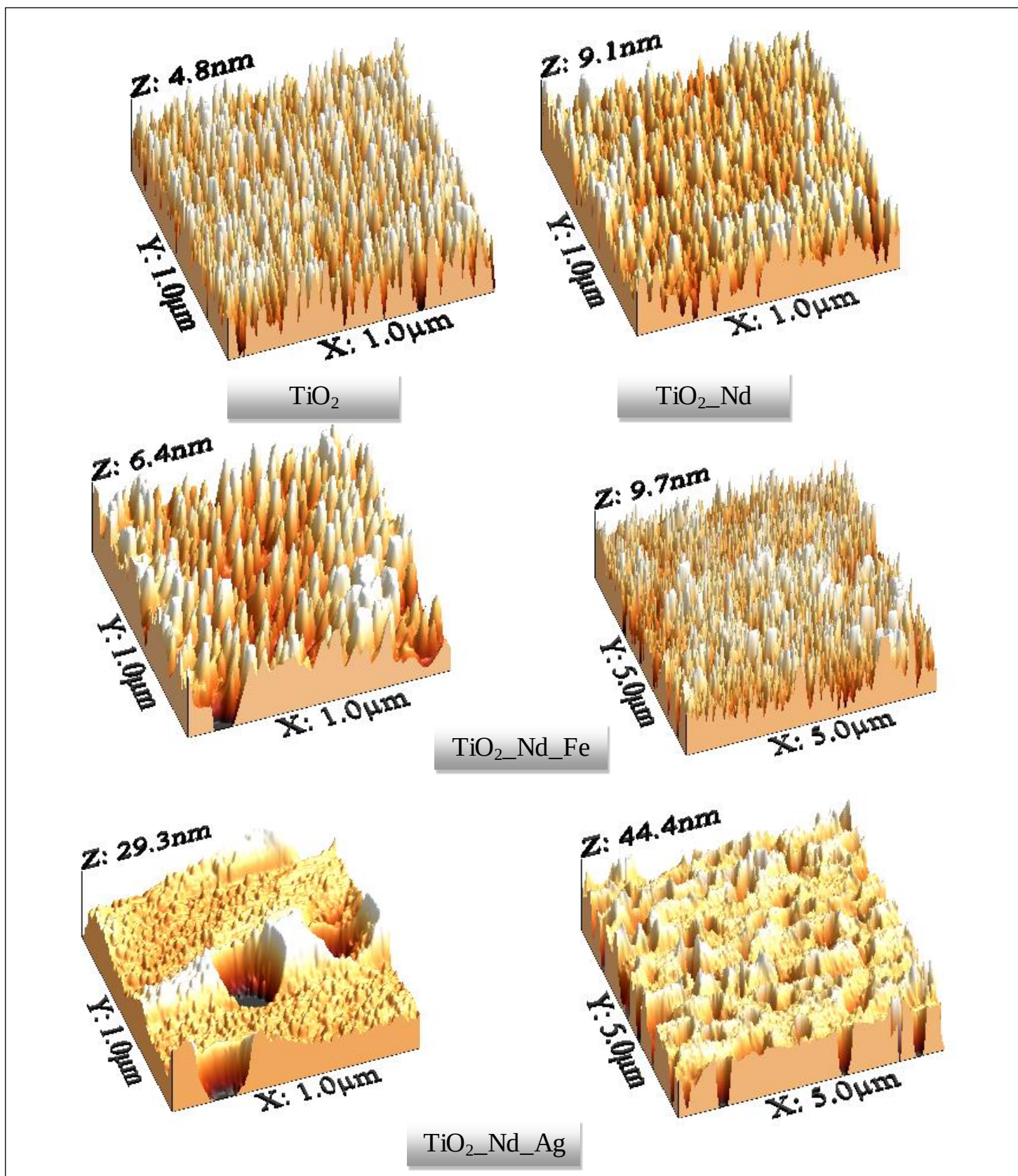
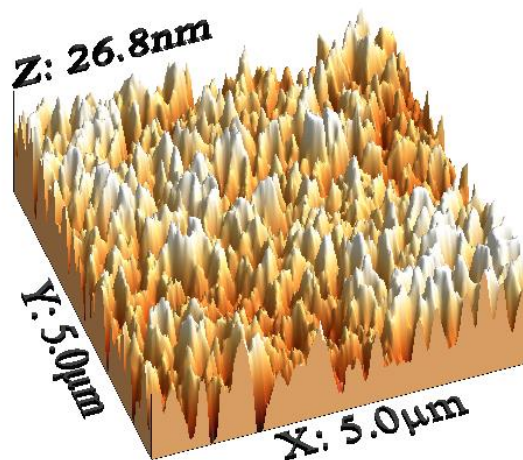
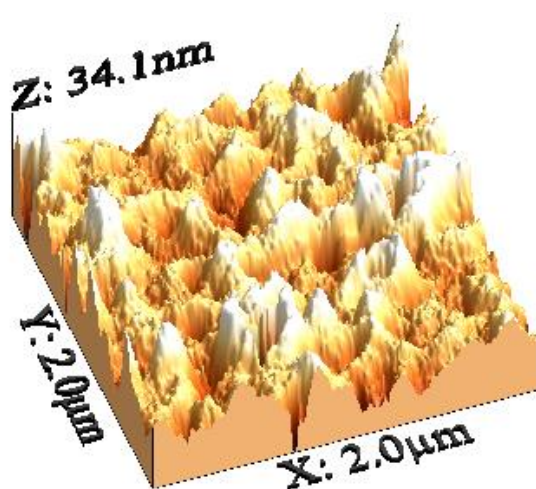
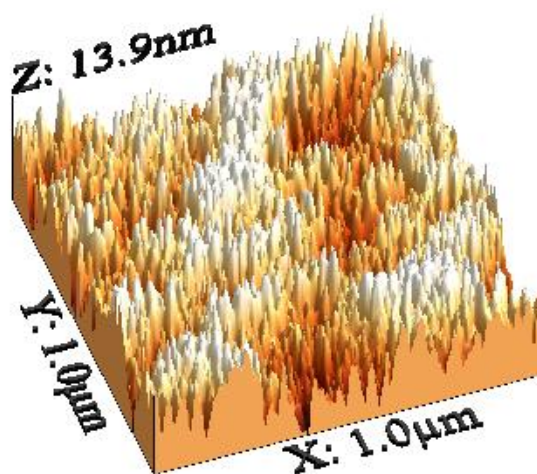


Figure 33

AFM 3D Images of Nd-M (Fe, Ag, Cu & Cd) doped TiO₂



TiO_2NdCu



TiO_2NdCd

Figure 33 (continued)

AFM 3D Images of Nd-M (Fe, Ag, Cu & Cd) doped TiO_2

Table 4
Roughness parameters of the TiO₂ films obtained by AFM image processing

Compound	Roughness R _a (nm)	Roughness R _{ms} (nm)	Skewness R _{sk}	Kurtosis R _{ku}
TiO ₂	1.13	0.91	0.12	2.62
TiO ₂ _Nd	1.82	1.46	0.12	2.63
TiO ₂ _Nd_Fe	1.52	1.23	0.34	2.52
TiO ₂ _Nd_Cu	6.51	5.00	-0.19	3.44
TiO ₂ _Nd_Ag	5.54	3.63	-0.19	4.87
TiO ₂ _Nd_Cd	3.34	2.73	-0.11	2.41

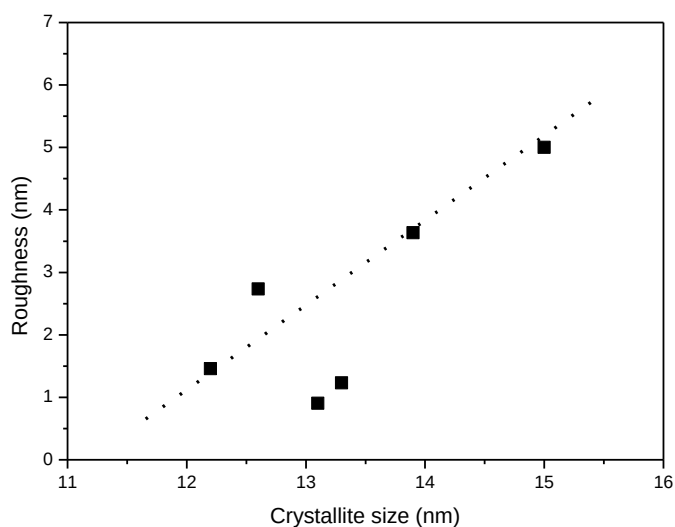


Figure 34
Relation between Roughness and Crystallite size

In addition, from literature, for the Cd doped TiO₂ films, a direct relationship between the crystallite size and roughness was obtained; the roughness increases with increasing the crystallite size and same relation occurs in this study (Andronic, L. et al., 2009).

4.3 Optical Properties by Photoluminescence

4.3.1 Fluorescence mechanisms in semiconductors:

Electrons (e-) and holes (h+) created by the absorption of photons with energy $\hbar \omega_{\text{exc}} > E_g$ are showed in figure 35 as shaded area at the bottom of the conduction band (CB) and the empty states at the top of the valence band (VB). The flow of transitions within CB and VB represents the quick thermalization of the excited (e-) and (h+) through phonon emission. Direct and indirect gap material located at the left and right side respectively in figure 35. For the direct gap, the CB minimum and the VB maximum occur at the same k values. The (e-) and (h+) recombination ,which represent the photon absorption and emission processes, can conserve momentum without the assistance of phonons, since the momentum of the electron is much higher than the momentum of the absorbed or emitted photon. Thus, vertical arrows on E-k diagrams represent photon absorption and emission processes. For indirect gap material, the CB minimum and the VB maximum occur at different k values. Therefore, in momentum conservation, the process of photon absorption must be carried out involving either a phonon absorption (with “+” sign as indication) or a phonon emission (with “-” sign as indication). The process of PL requires a phonon emission. The peak energy of the PL roughly reflects its band gap since the phonon’s energy (~ 0.01 eV) is much smaller than the PL photon’s energy. (Ned.ipac.caltech.edu, 2017).

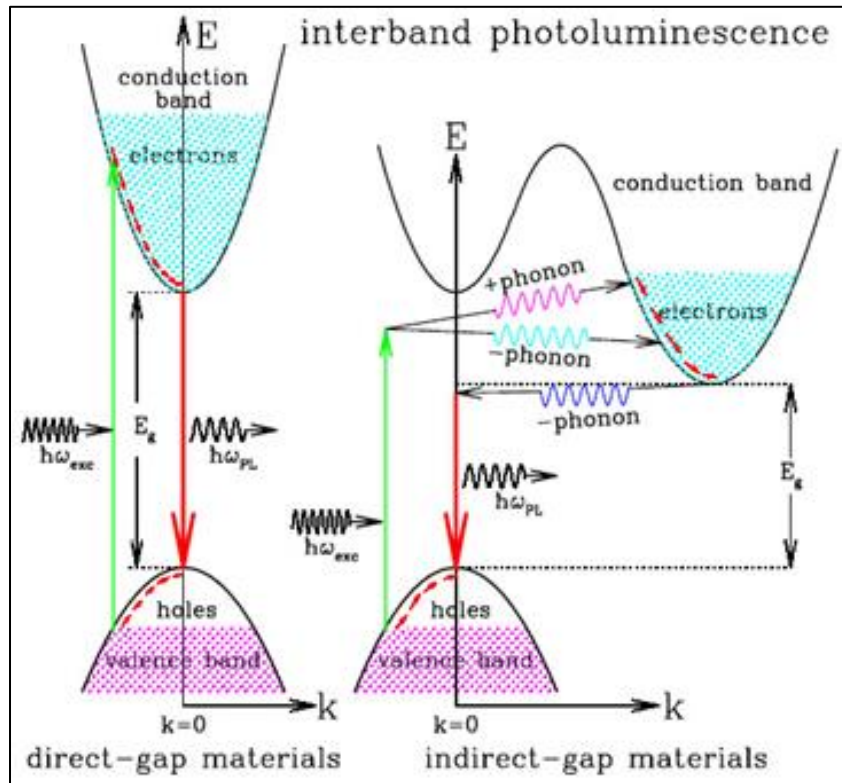


Figure 35

Energy levels in the direct and indirect gap materials

4.3.2 Photoluminescence Results and discussion:

The fluorescence spectra obtained in Nd-M(Fe, Cu, Ag and Cd) co-doped TiO_2 thin films are shown in figure 36.

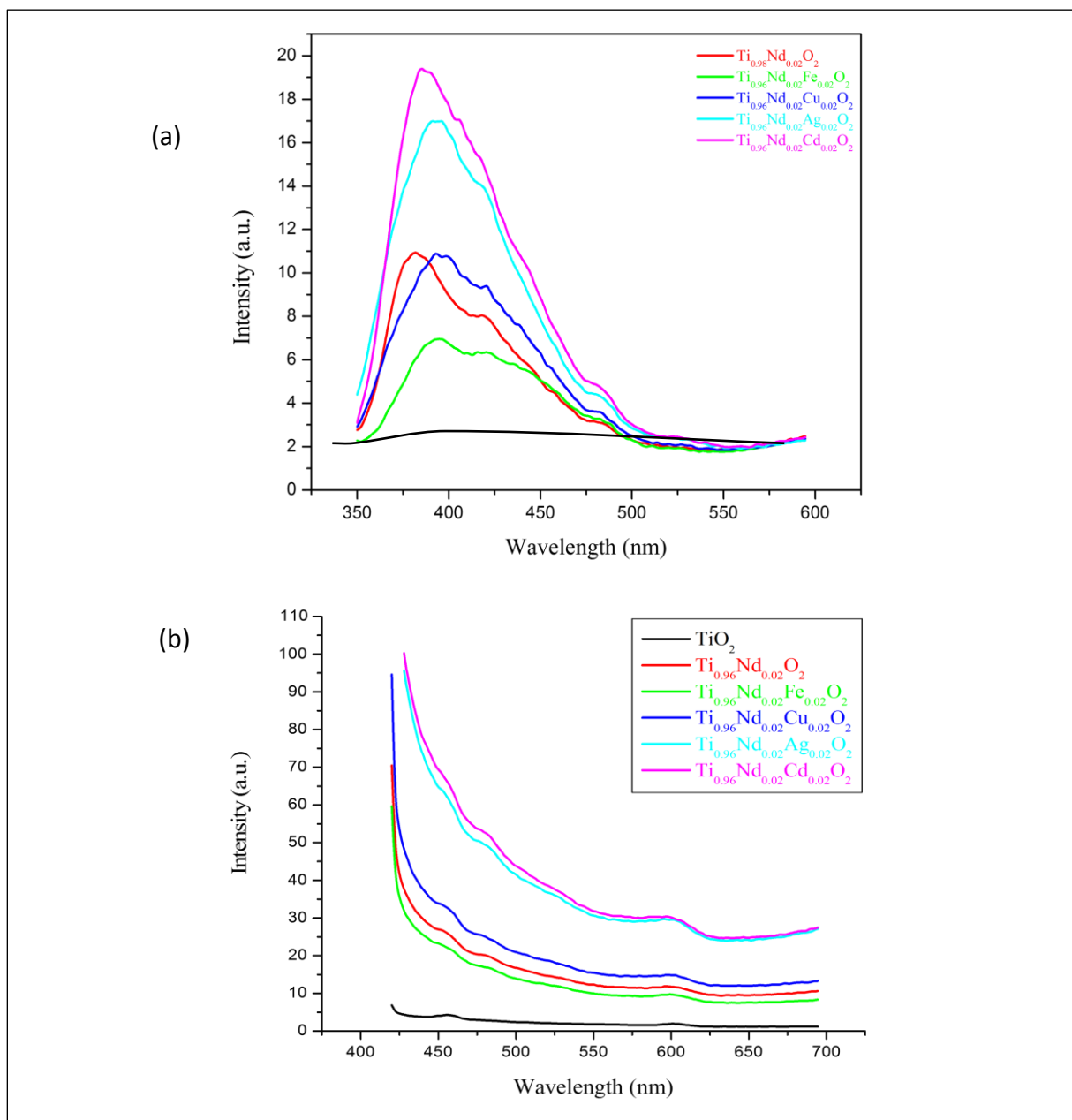


Figure 36

Photoluminescence spectra of Nd-M (Fe, Cu, Ag & Cd) doped TiO_2

(a) range: 350 to 600 nm (b) range: 450 to 700 nm

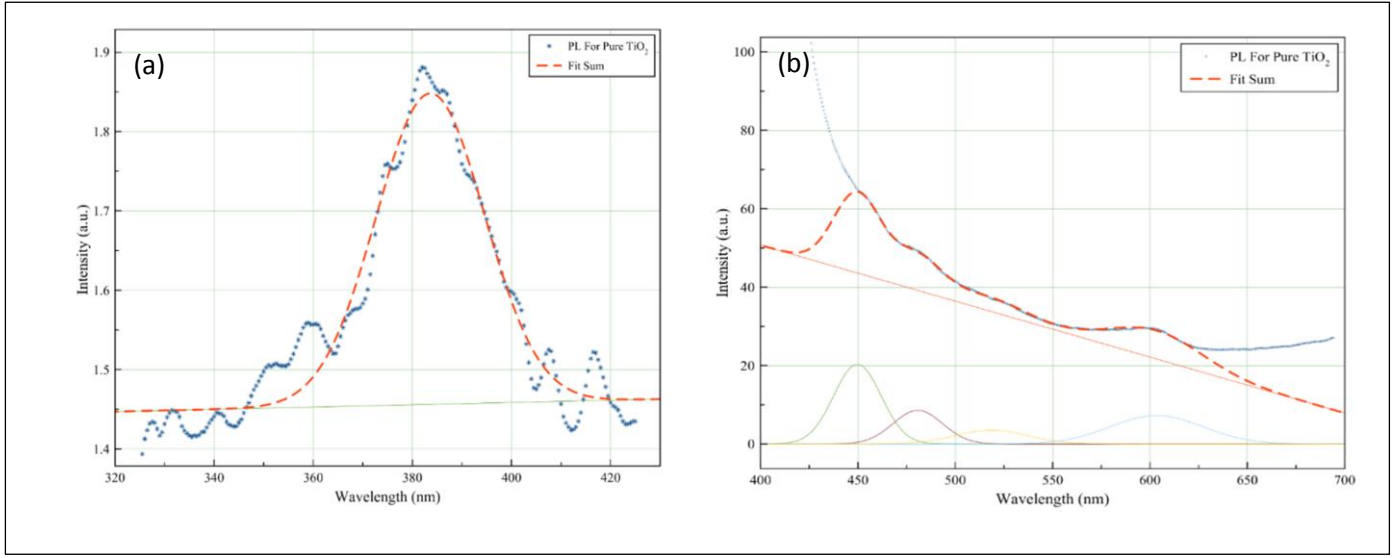


Figure 37

PL spectra of Pure TiO₂ thin film (a) range: 350 to 600 nm

(b) range: 450 to 700 nm

PL spectra of pure TiO₂ thin film are shown in Figures 37. The PL spectra are a sum of several Gaussian peaks that illustrate the defect energy levels. The peak in Fig.37 (a) related to Ti (acceptors) and other peaks in Fig. 37 (b) related to O (donors). These first peak indicate the band gap energy which is equal to 3.23eV. The other small peaks specifies the defect levels that occurs in TiO₂.

Figure 38 shows the proposed energy diagram for pure TiO₂, drawn based on the Gaussian packs positions as shown before. The major defects, in orange lines, represent:

O vacancies (donors): F, F⁺ and F⁺⁺ (or O_v, O_v⁺ and O_v⁺⁺).

Ti vacancies or other (acceptors): Neutral acceptor A⁰

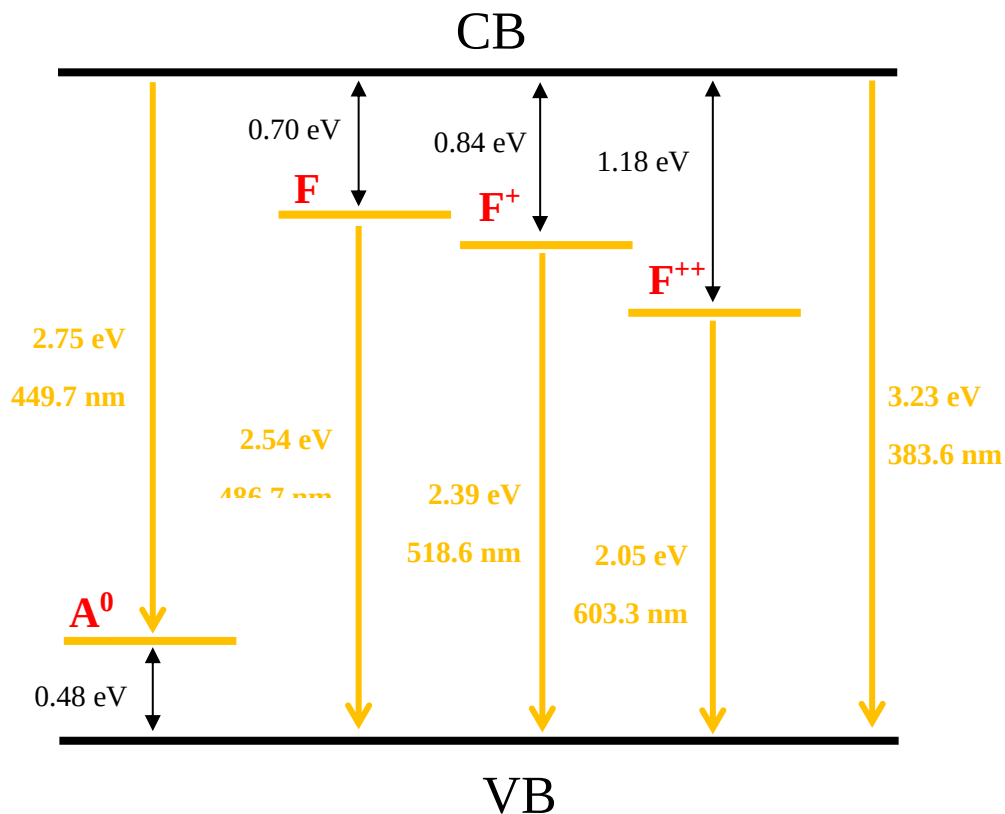


Figure 38

Energy diagram for pure TiO₂

For all energy diagrams, the conversion from eV to nm made by using the following approximate formula:

$$\text{Wavelength (nm)} \times \text{Energy (eV)} = 1240.$$

The indirect band gap of anatase means that the phonons are involved in the transitions, which indicate that, the transitions not vertical in k-space.

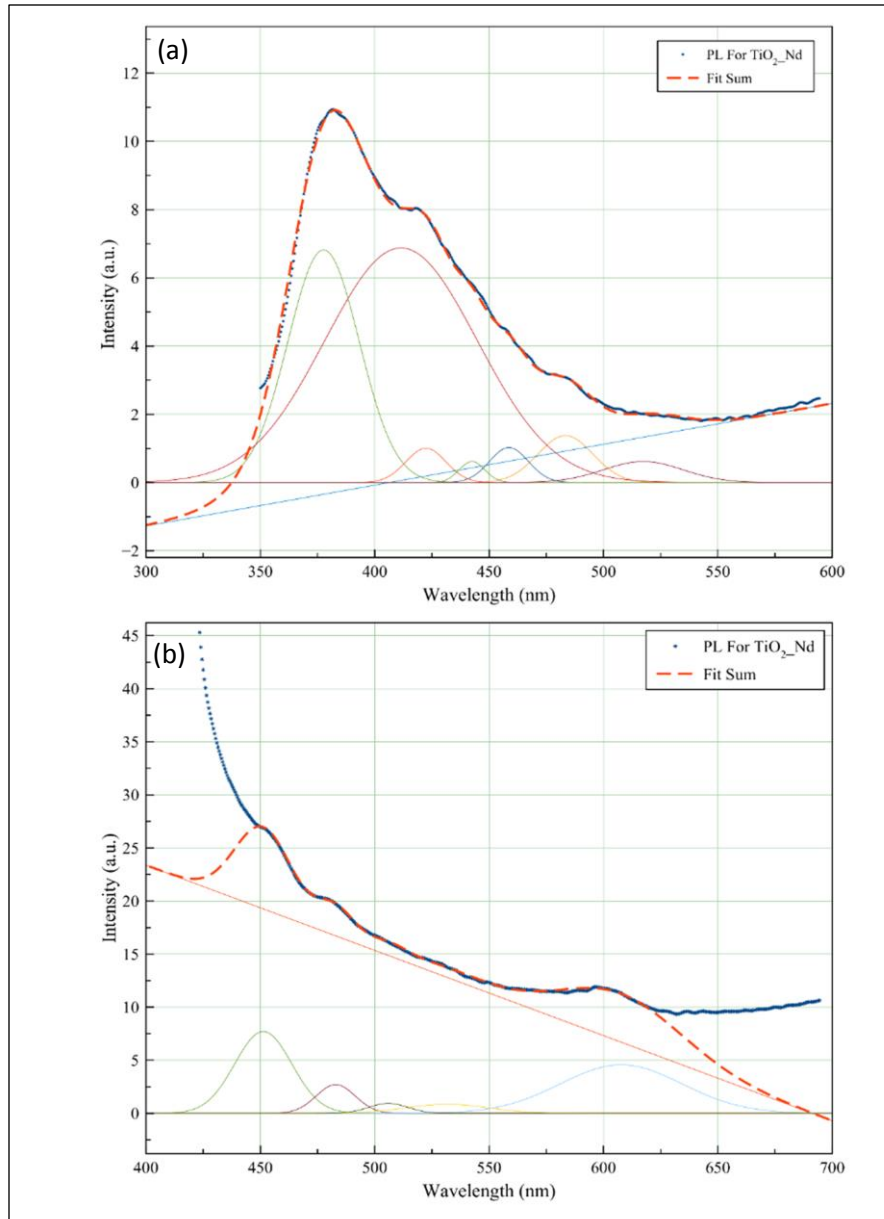


Figure 39

PL spectra of (Nd) doped TiO₂ thin film (a) range: 350 to 600 nm

(b) range: 450 to 700 nm

Figures 39 show PL spectra of Nd-doped TiO₂ thin film with Gaussian fitting. The maximum peak is located at 377.6 nm, hence the band gap energy is equal to 3.28 eV. The observed peaks helps in drawing the proposed energy diagram of Nd-doped TiO₂ as shown in Figure 40. Nd

states related to $\text{Nd}^{3+} 4f$ or other Nd induced defects (shallow donors) drawn in blue lines.

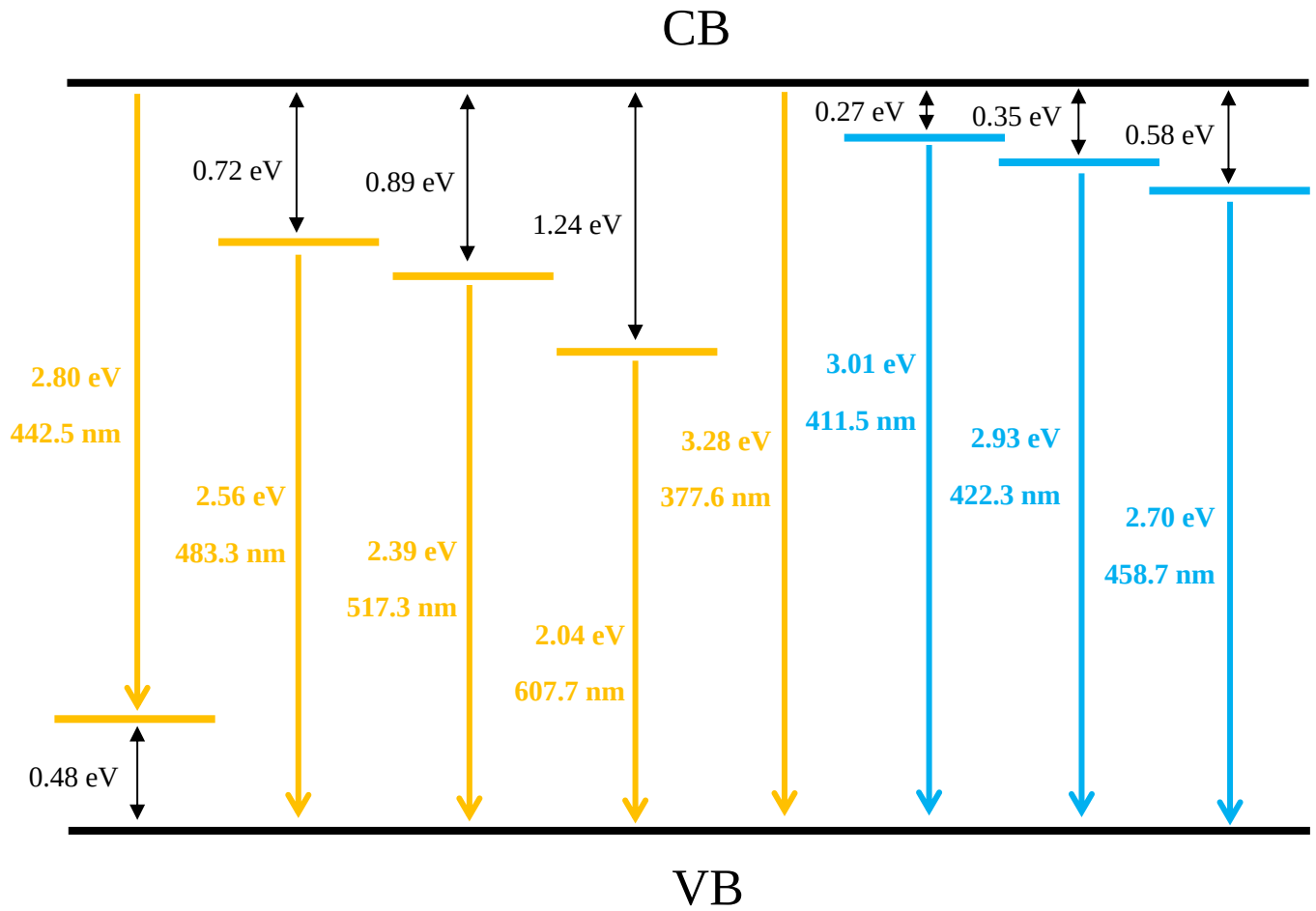


Figure 40
Energy diagram for Nd-doped TiO_2

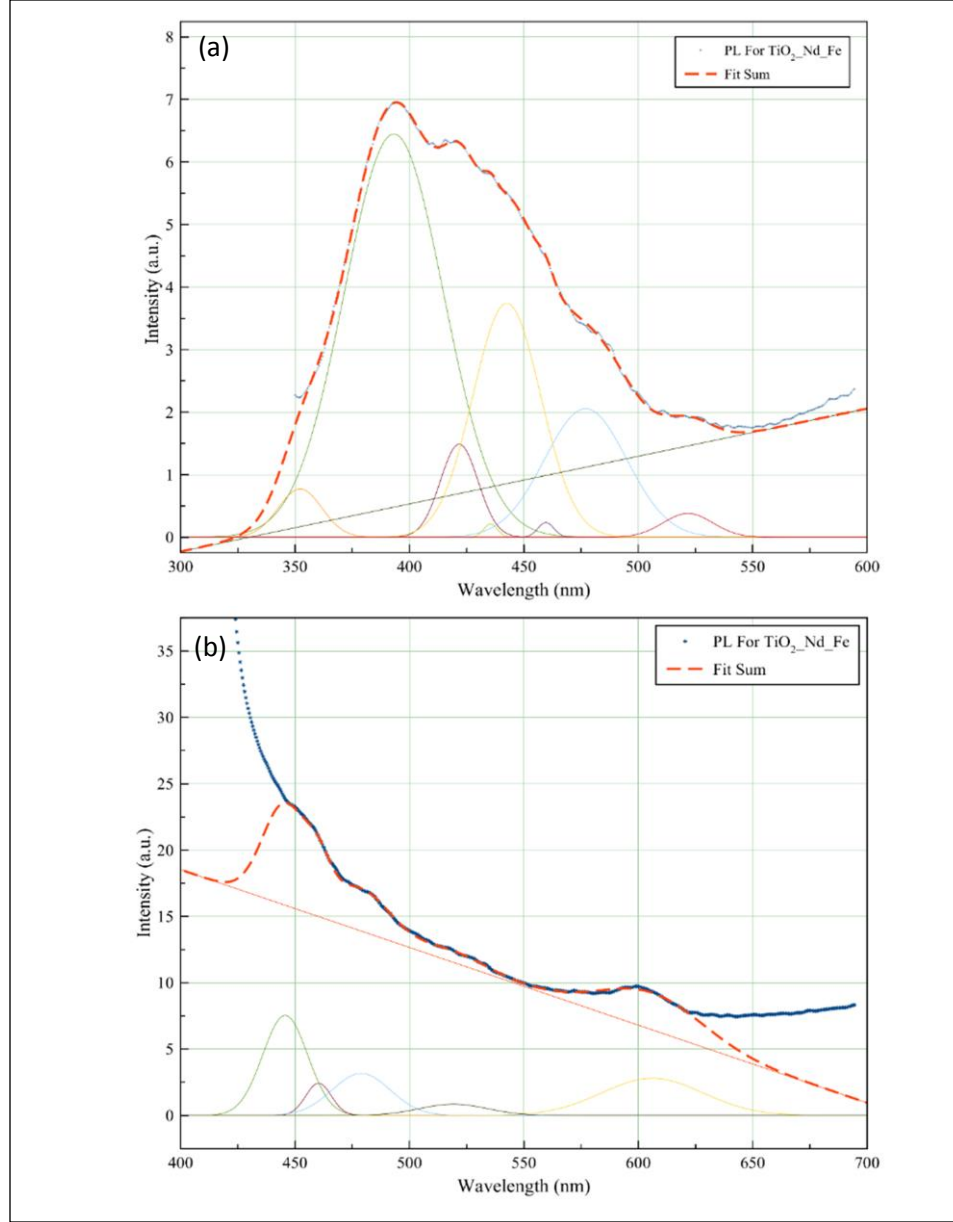


Figure 41

**PL spectra of (Nd,Fe) co- doped TiO₂ thin film (a) range: 350 to 600 nm
(b) range: 350 to 600**

Figures 41 show PL spectra of (Nd,Fe) co-doped TiO₂ films fitted with Gaussian curves. The band gap energy is equal to 3.15 eV and the proposed energy diagram is shown in Figure 42. Fe in TiO₂ works as acceptor states and Fe-induced transitions as shown in green lines.

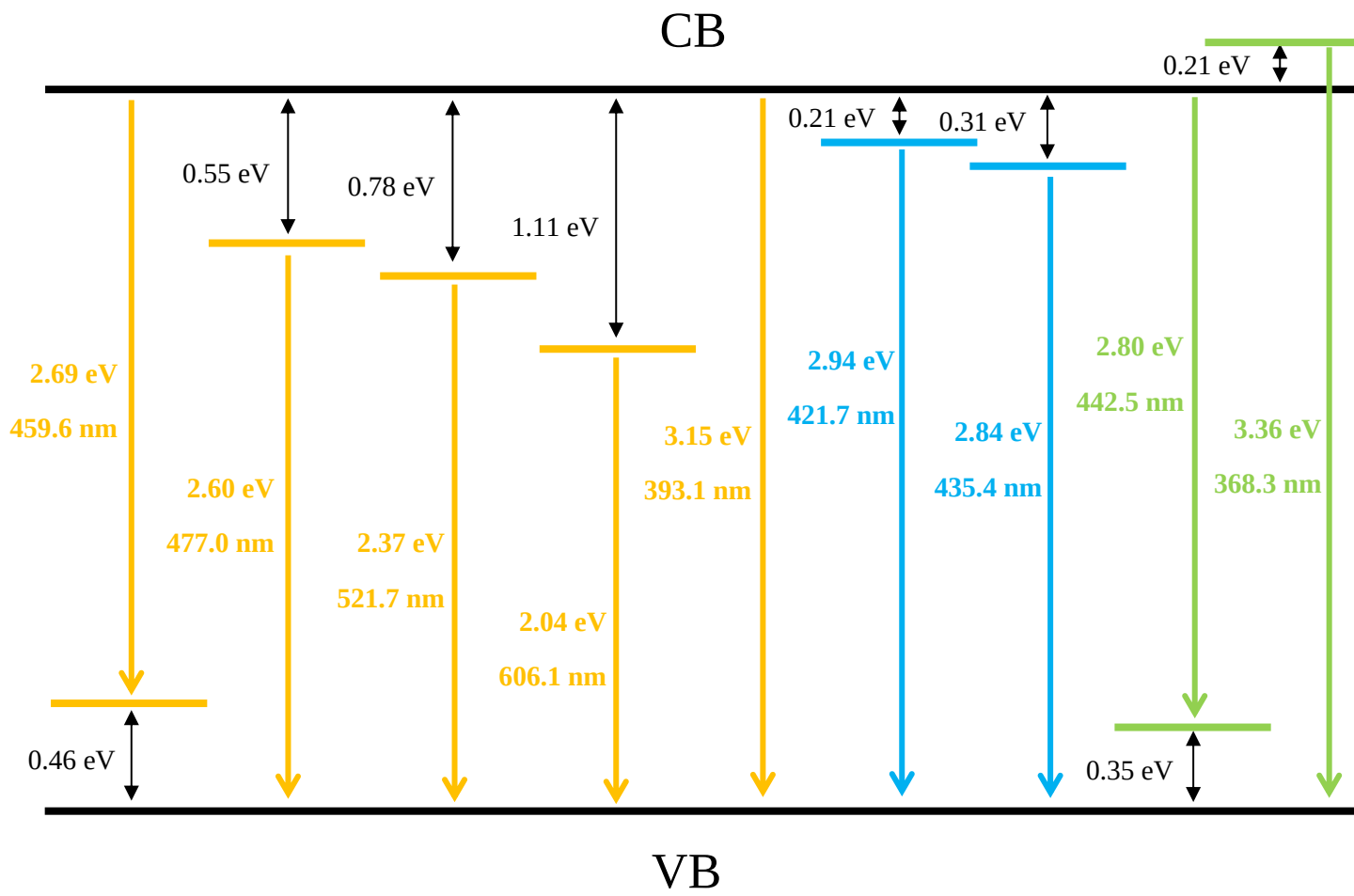


Figure 42
Energy diagram for (Nd,Fe) co-doped TiO₂

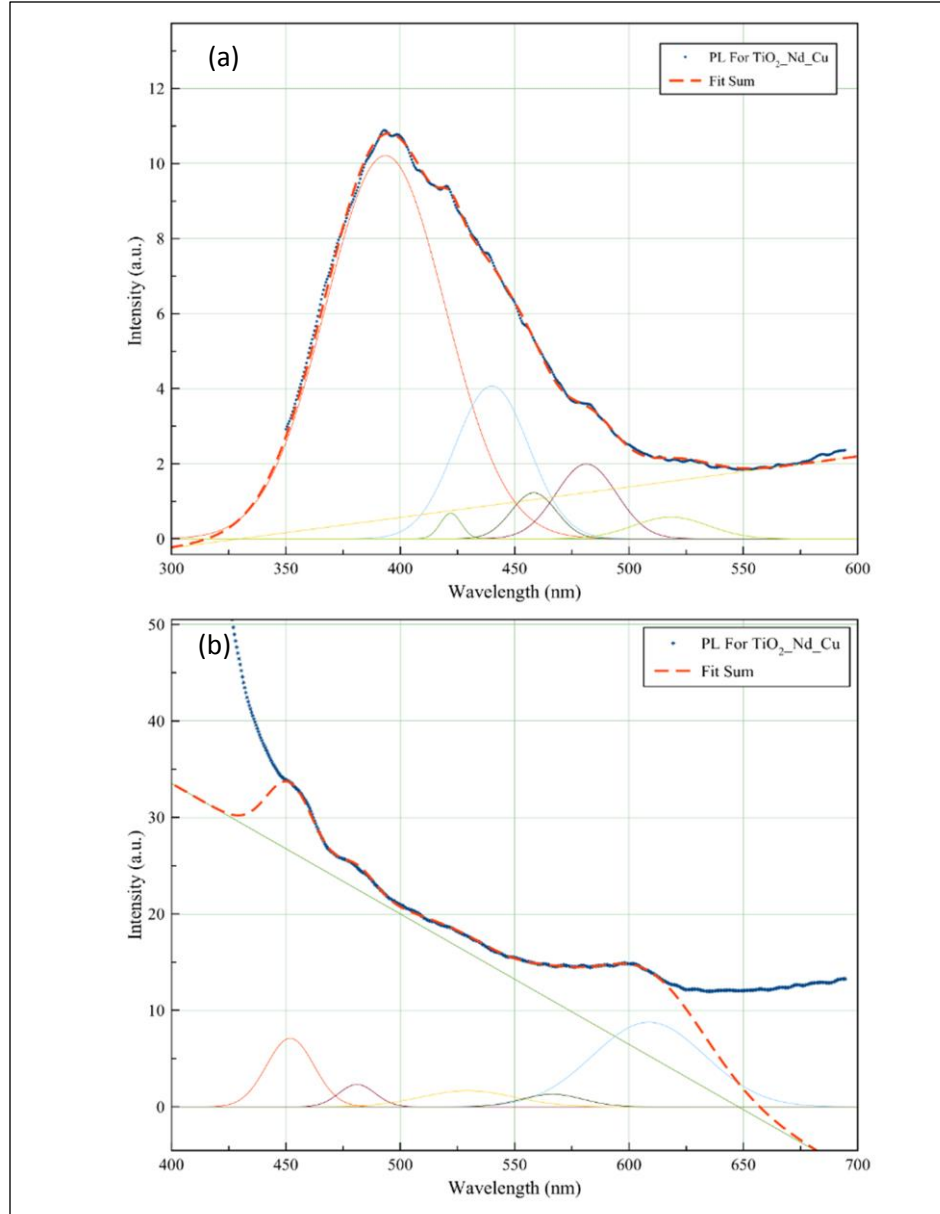


Figure 43

**PL spectra of (Nd,Cu) co-doped TiO₂ thin film (a) range: 350 to 600 nm
(b) range: 450 to 700 nm**

For (Nd,Cu) co-doped TiO₂, the PL spectra are shown in Figures 43. The highest at wavelength 393.5 nm corresponds to a band gap energy of 3.15 eV as shown in Figure 44. Cu in energy diagram shallow (donors) states as shown in magenta line.

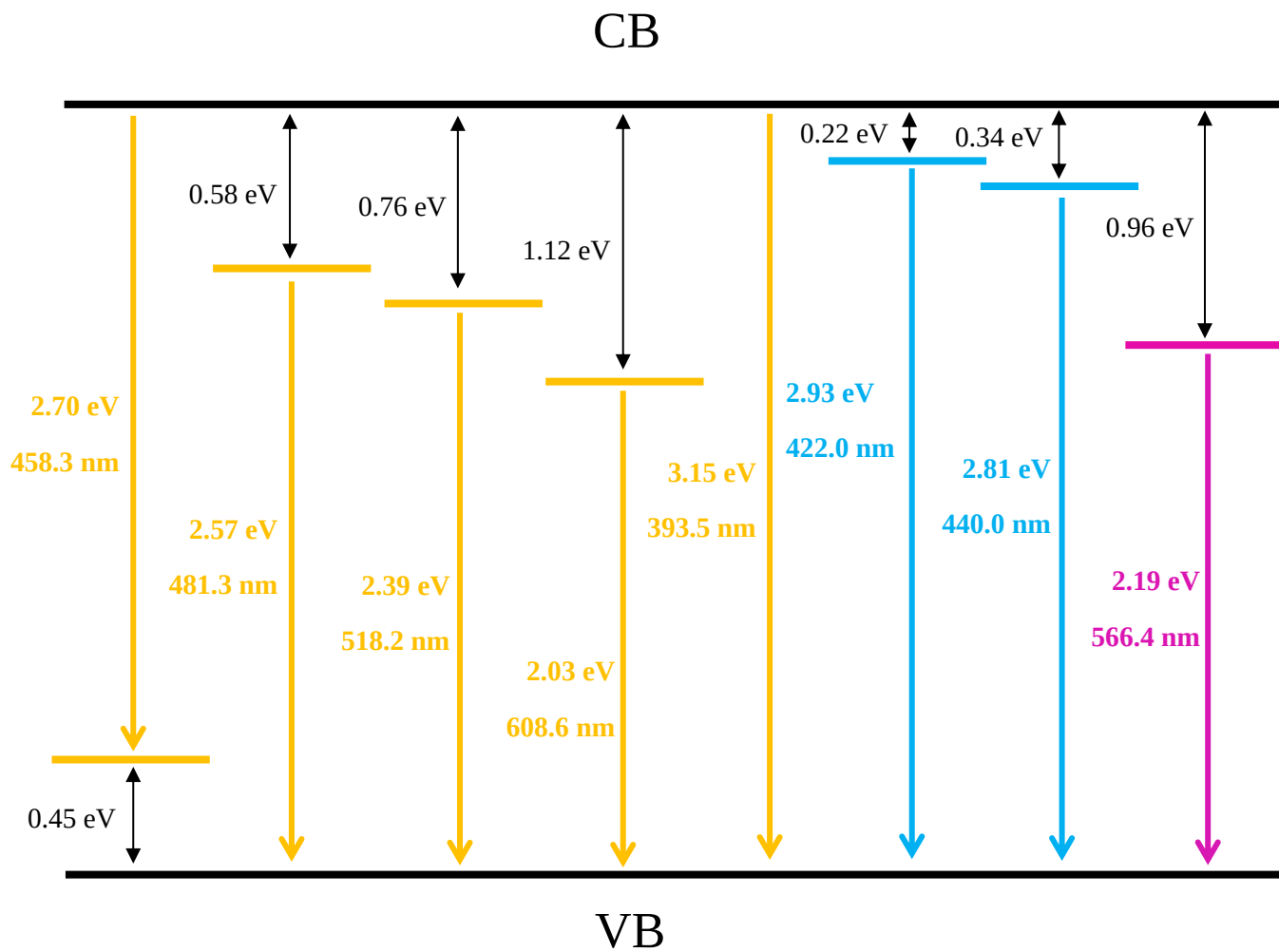


Figure 44
Energy diagram for (Nd,Cu) co-doped TiO₂

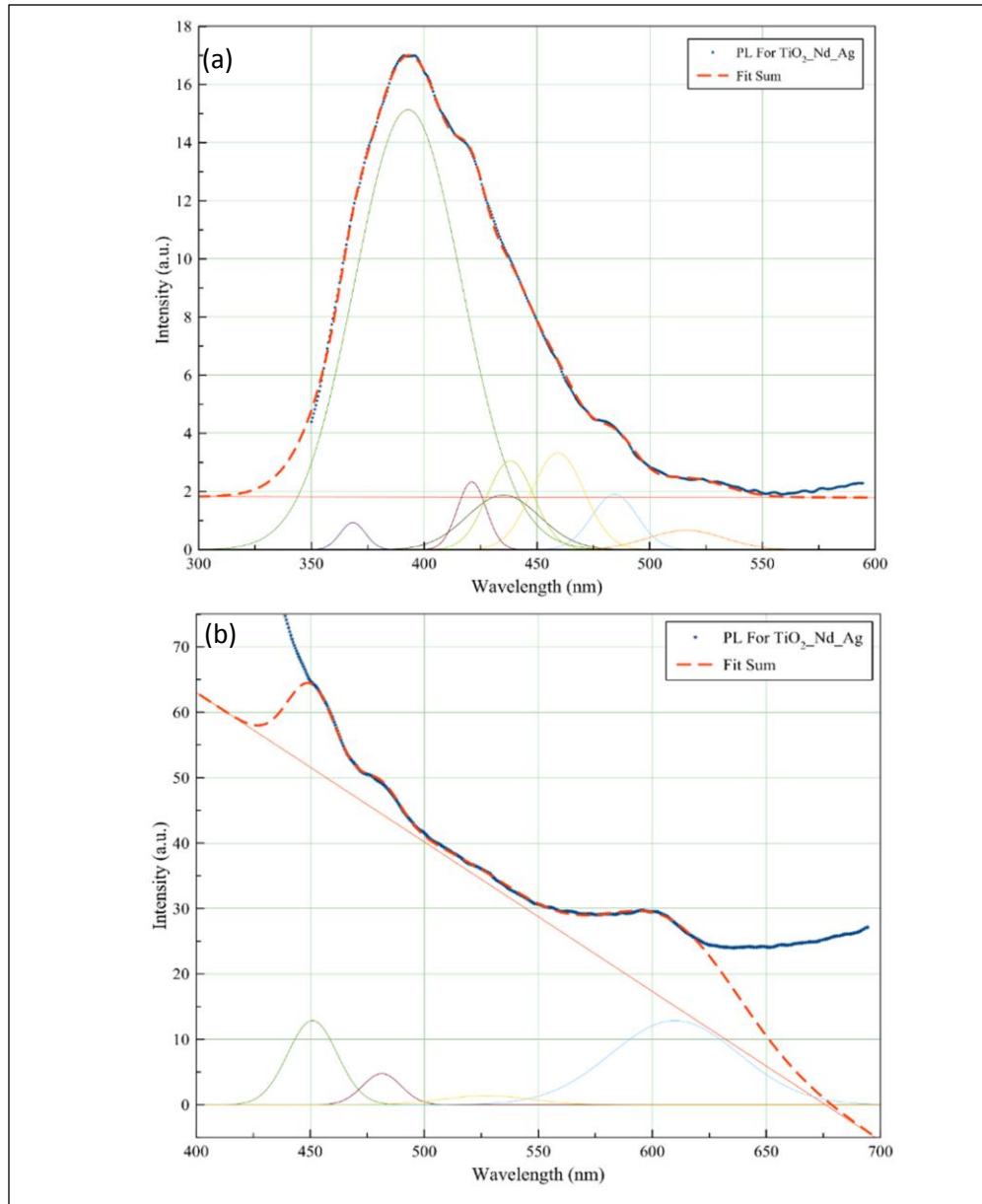


Figure 45

**PL spectra of (Nd,Ag) co-doped TiO₂ thin film (a) range: 350 to 600 nm
(b) 450 to 700 nm**

Figures 45 show PL spectra of (Nd,Ag) co-doped TiO₂ thin films and the corresponding band gap energy of is equal to 3.15 eV. Ag in TiO₂, shown in Figure 46, represents acceptor states with Ag induced transitions as shown in red lines.

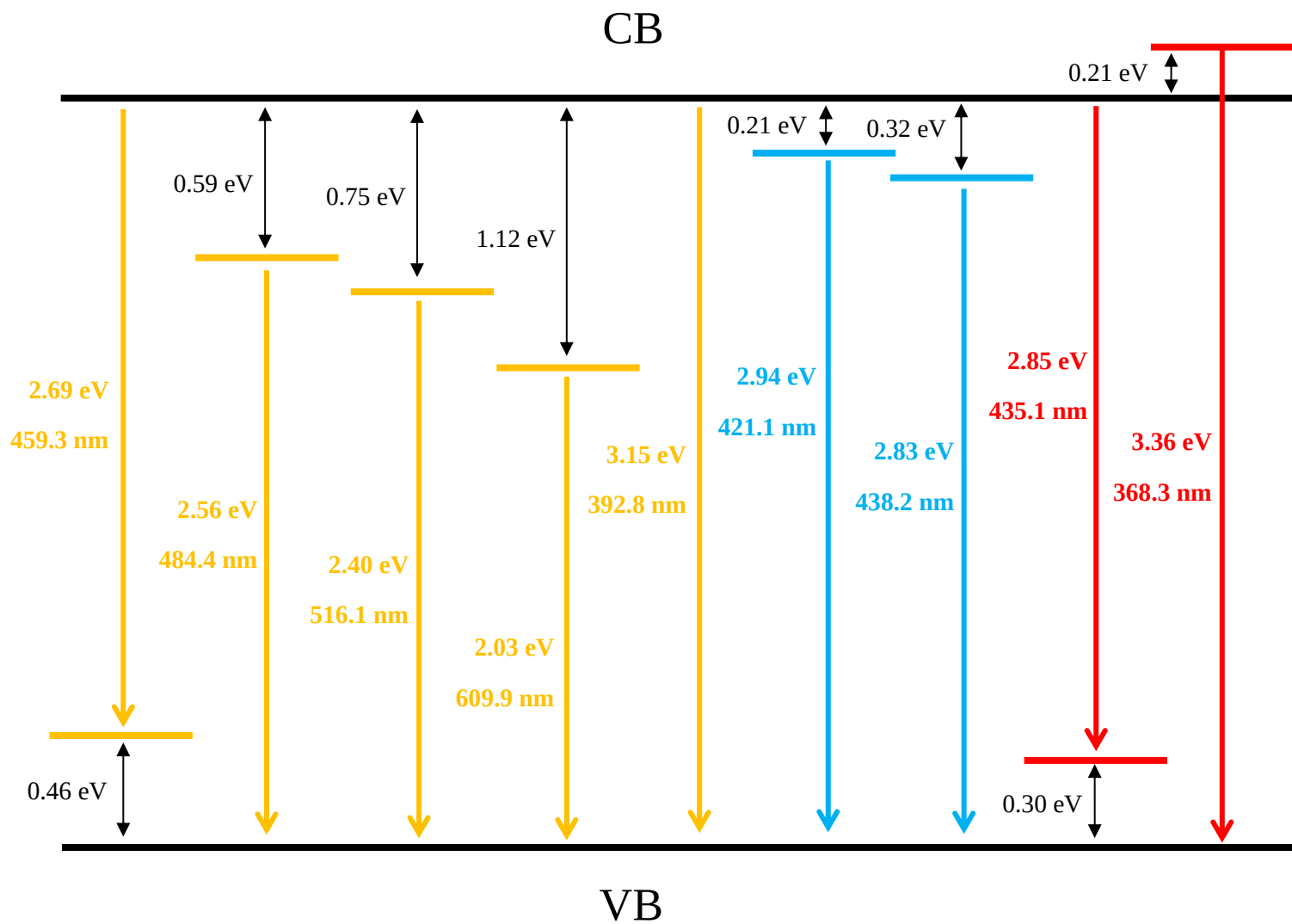


Figure 46

Energy diagram for (Nd,Ag) co-doped TiO₂

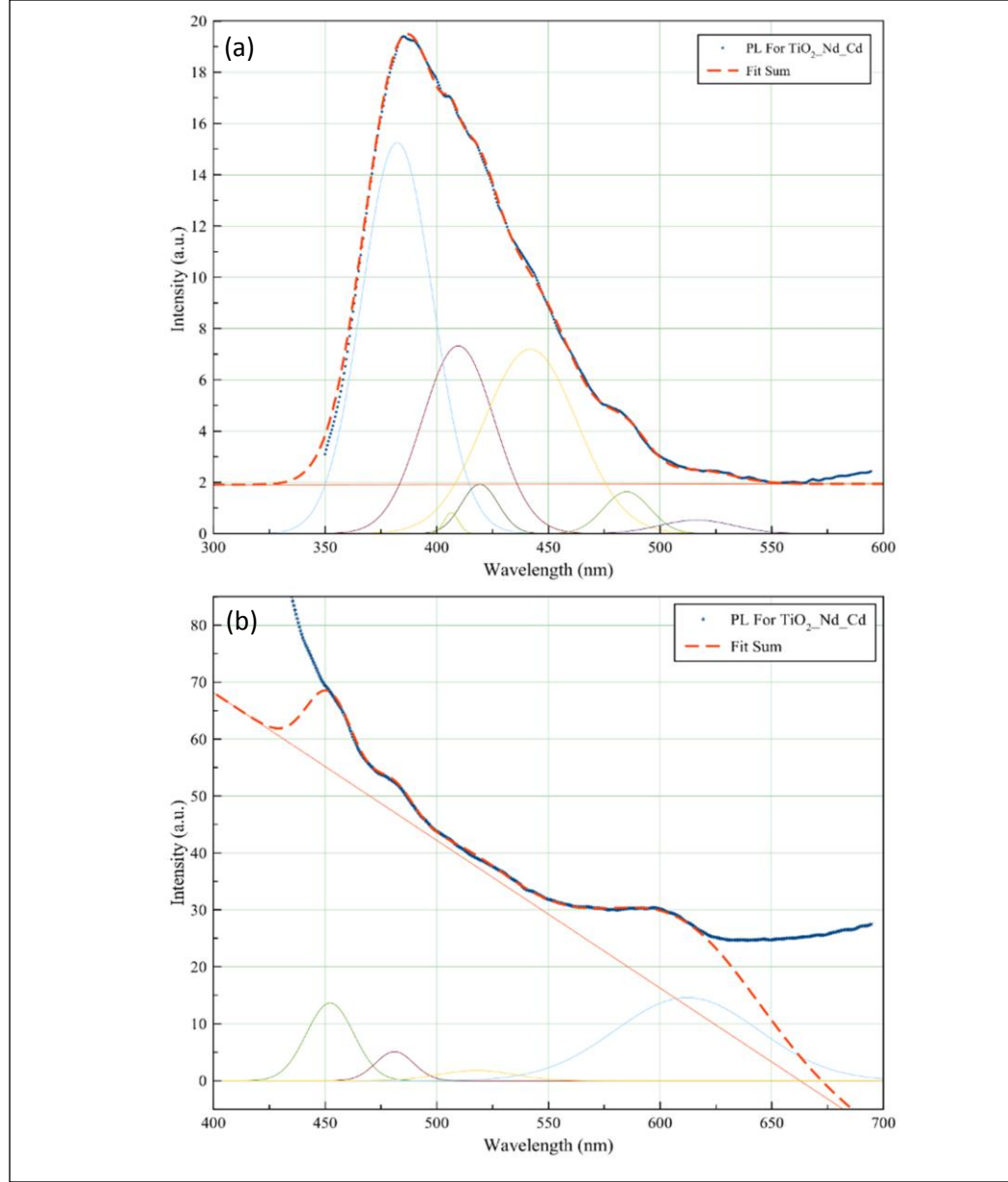


Figure 47

**PL spectra of (Nd,Cd) co-doped TiO₂ thin film (a) range: 350 to 600 nm
(b) range: 450 to 700**

Finally, (Nd,Cd) co-doped TiO₂ thin films PL spectra are shown in Figures 47. The maximum peak placed at 382.3 nm indicates a band gap energy equal to 3.24 eV as drawn in Figure 48. Cd in TiO₂ represents shallow donor (probably) states as indicates in violet line.

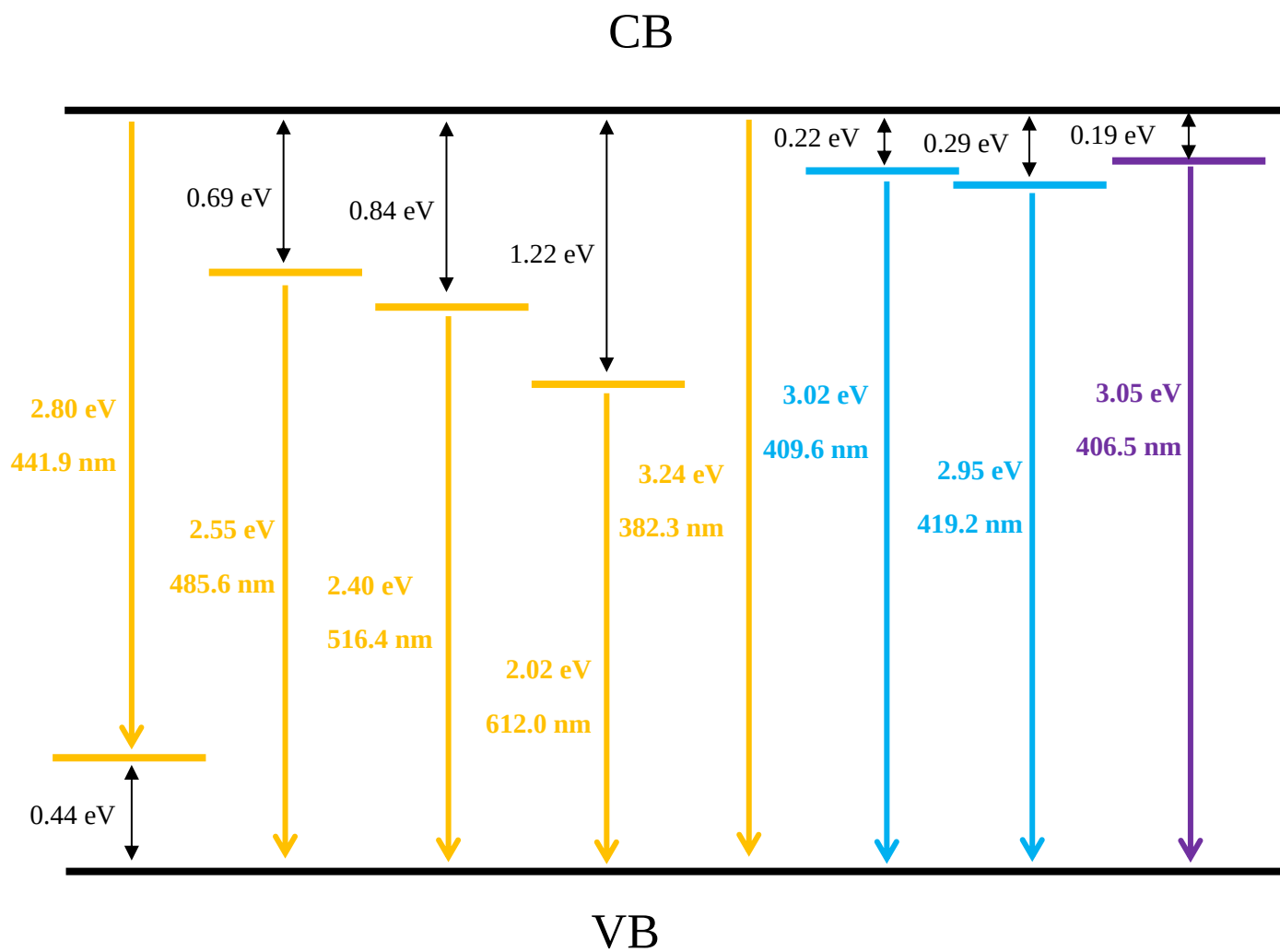


Figure 48
Energy diagram for (Nd,Cd) co-doped TiO₂

Table 5
Band gap energy for Nd-M (Fe,Cu,Ag and Cd) co-doped
TiO₂ thin films

Sample	Wavelength (nm)	Band Gap Energy (eV)
TiO ₂	383.6	3.23
TiO ₂ _Nd	377.6	3.25
TiO ₂ _Nd_Fe	393.1	3.14
TiO ₂ _Nd_Cu	393.5	3.16
TiO ₂ _Nd_Ag	392.8	3.17
TiO ₂ _Nd_Cd	382.3	3.22

Table 5 shows the wavelength of the highest peak and calculated band gap energy. Nd doped TiO₂ thin film has the highest band gap energy, while (Nd, Fe) co-doped TiO₂ has the lowest band gap energy.

4.4 UV-Visible Absorption Spectroscopy

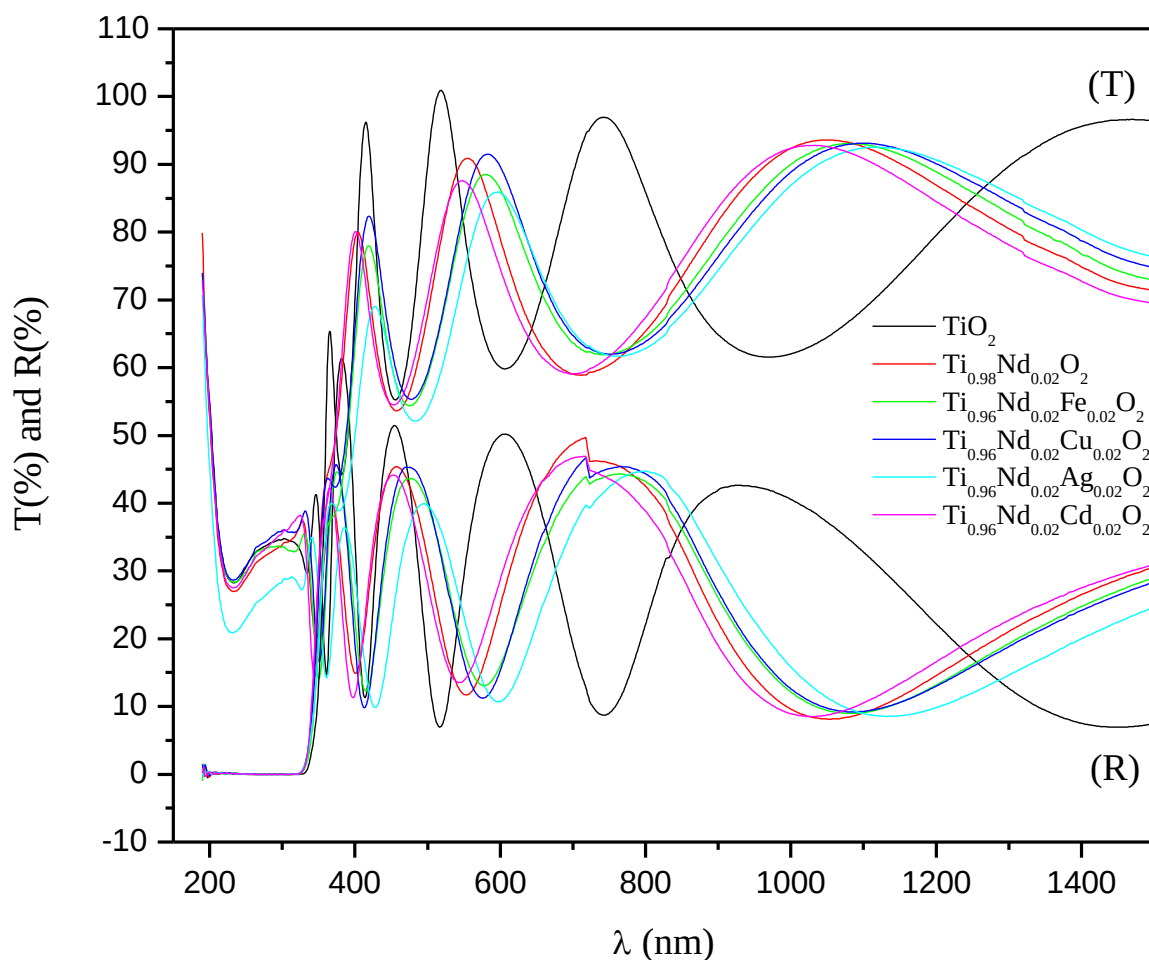


Figure 49

Optical Transmittance $T(\lambda)$ and Reflectance $R(\lambda)$ Spectral of Nd-M (Fe, Cu, Ag & Cd) co-doped TiO_2 thin films.

The spectral optical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ of Nd-M(Fe, Cu, Ag and Cd) co-doped TiO_2 thin films are shown in Figure 49. The spectra reveal very pronounced interference effects in the transparency region 350– 1500 nm with sharp fall of transmittance at the band edge. It is important to highlight that the appearance of interferences is an indication of the good homogeneity of the deposited films thickness.

The spectral absorbance $A(\lambda)$ is calculated from the experimental data by using the following equation (4) (Bensouici, F. et al., 2015):

$$A(\lambda) = \ln \left[\frac{1-R(\lambda)}{T(\lambda)} \right] \quad (4)$$

where $R(\lambda)$ is reflectance and $T(\lambda)$ is transmittance.

The absorbance is related to the absorption coefficient α , as $\alpha = A/d$, where d is the film thickness. The optical indirect bandgap E_g is then determined from the well-known energy-exponential relation (5) (Bensouici, F. et al., 2015):

$$AE = A_{Op}(E - E_g)^2 \quad (5)$$

where A_{Op} is a constant for each film.

By using Equations 4 and 5, the plot of $(\alpha E)^{0.5}$ vs. E as shown in Fig. 50 using the Tauc method, gives the indirect bandgap (E_g) value. The energy bandgap varies with Nd-M(Fe, Cu, Ag, Cd)-dopant in the range 3.23–3.34 eV.

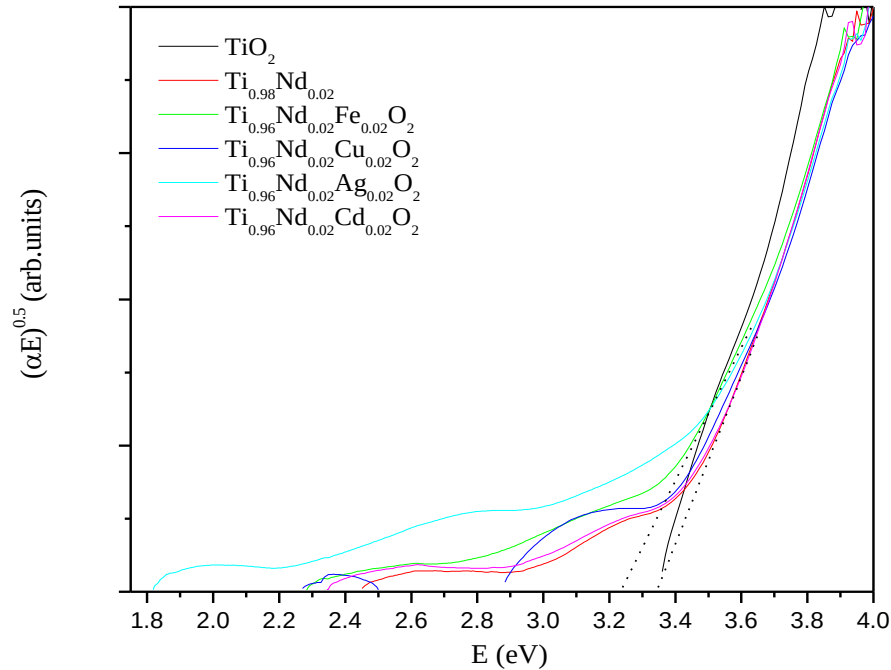


Figure 50

Optical gap of Nd-M (Fe, Cu, Ag & Cd) co-doped TiO₂ thin films.

Table 6
Band gap energy calculated from Uv-vis and PL methods

Sample	Band Gap Energy (eV) From Uv-vis	Band Gap Energy (eV) From PL
TiO ₂	3.33	3.23
TiO ₂ _Nd	3.34	3.25
TiO ₂ _Nd_Fe	3.26	3.14
TiO ₂ _Nd_Cu	3.29	3.16
TiO ₂ _Nd_Ag	3.23	3.17
TiO ₂ _Nd_Cd	3.34	3.22

As shown in table 6, the band gap energy measured from Uv-vis spectroscopy is little bit higher than the band gap energy calculated using PL for all films, which means that there is a shift in the energy gap value between these two methods.

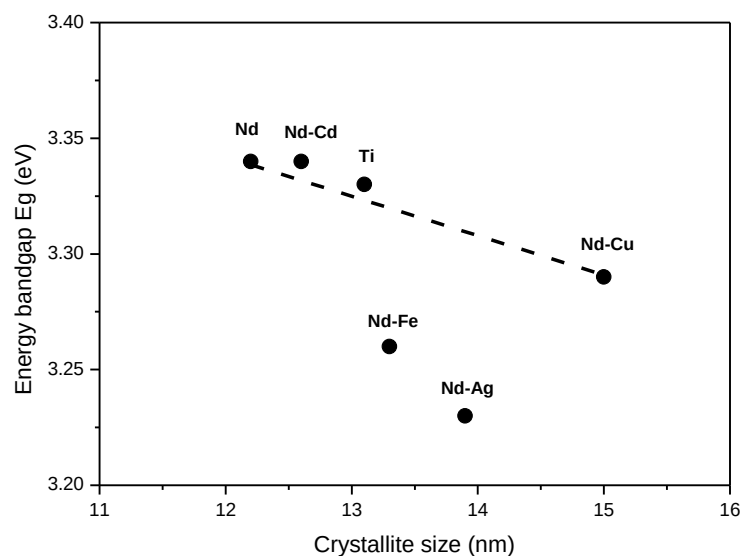


Figure 51

**Variation of energy bandgap Eg as function of crystallite size of Nd-M
(Fe, Cu, Ag & Cd) co-doped TiO₂ thin films**

Figure 51 show the existence of a good correlation between the energy bandgap of some points and the crystallite size. The dispersion of (Nd,Fe) and (Nd,Ag) from the linear fit may be due to several factors, including: (i) for Ag-doped TiO_2 it was found that Ag has the tendency to form nano-clusters of Ag dispersed homogeneously over the film surface (Bensouici, F. et al., 2015); (ii) the surface roughness and skewness (Nd,Fe) has the highest value of 0.34; (iii) in this study, an average thickness of 250 nm was used for all films, but in reality, it may vary for each film; (iv) etc.

Table 7

Comparing different parameters between literature and this study

Thin film Composition	Method of deposition	CS (nm)	E _g (eV)	Dye & time	PCE (%)		k (min ⁻¹)	Reference
TiO₂	Sol-gel dip-coating	13.1	3.33	RhB 4 h	75		0.00631	This study
Ti_{0.98}Nd_{0.02}O₂		12.2	3.34		45		0.00279	
Ti_{0.96}Nd_{0.02}Fe_{0.02}O₂		13.3	3.26		20		0.00118	
Ti_{0.96}Nd_{0.02}Cu_{0.02}O₂		15.0	3.29		28		0.00145	
Ti_{0.96}Nd_{0.02}Ag_{0.02}O₂		13.9	3.23		38		0.00228	
Ti_{0.96}Nd_{0.02}Cd_{0.02}O₂		12.6	3.34		29		0.00148	
TiO₂	Sol-gel method	22.6	2.74	MO 3 h	20			Tang, W. et al., 2014
TiO₂-0.1%Fe		19.1	2.64		14			
TiO₂-0.2%Fe		19.3	2.46		15			
TiO₂-0.5%Fe		19.3	2.35		15			
TiO₂-1%Fe		17.9	2.20		15			
TiO₂-2%Fe		19.7	2.05		16			
TiO₂	Sol-gel dip-coating	16	3.2	MB 3 h	92		0.015	Bensouici, F. et al., 2017
TiO₂-0.1%Cu		14.5	3.41		63			
TiO₂-0.2%Cu		16.3	3.40		48			
TiO₂-0.3%Cu		16.2	3.43		39			
TiO₂-2%Cu		14.4	3.42		30			
TiO₂-4%Cu		18.2	3.38		16		0.001	
TiO₂-6%Cu		15.6	3.22		16		0.001	
TiO₂-8%Cu		16.8	3.06					
TiO₂-10%Cu		16.8	3.31		16		0.001	
TiO₂	Sol-gel dip-coating	16	3.09	RhB 5 h	50		0.0021	Bensouici, F. et al., 2015
TiO₂-0.05%Ag		19	to3.31		80			
TiO₂-0.5%Ag							0.0048	
TiO₂-1%Ag					48		0.0024	
TiO₂-2%Ag		16			33		<0.0021	
TiO₂-3%Ag					20		<<0.0021	
TiO₂-4%Ag								
TiO₂-6%Ag		18						
TiO₂-10%Ag		17						
*	Doctor blade	Roughness		MO & MB	MO	MB		Andronic, L. et al., 2009
TiO₂			3.2					
TiO₂-0.1%A Cd		133.36	3.02		12.1	31.6		
TiO₂-0.5%A Cd		128.15	3.03		32.8	40.1		
TiO₂-1%A Cd		131.38	3.10		28.5	39.8		
TiO₂-0.1%C Cd		139.17	3.08		24.1	29.0		
TiO₂-0.5%C Cd		133.5	2.95		16.1	33.4		
TiO₂-1%C Cd		119.02	2.97		22.1	37.6		
		150.89			17.5	30.5		
TiO₂	Sol-gel method	20.759		MO 5 h	55			Bokare, A. et al., 2013
TiO₂-0.5%Nd		8.513			65			
TiO₂-1.0%Nd		7.598			82			
TiO₂-2.5%Nd		7.245			75			
TiO₂-5.0%Nd		6.211			50			

* A Cd Acetate precursor, C Cd Chloride

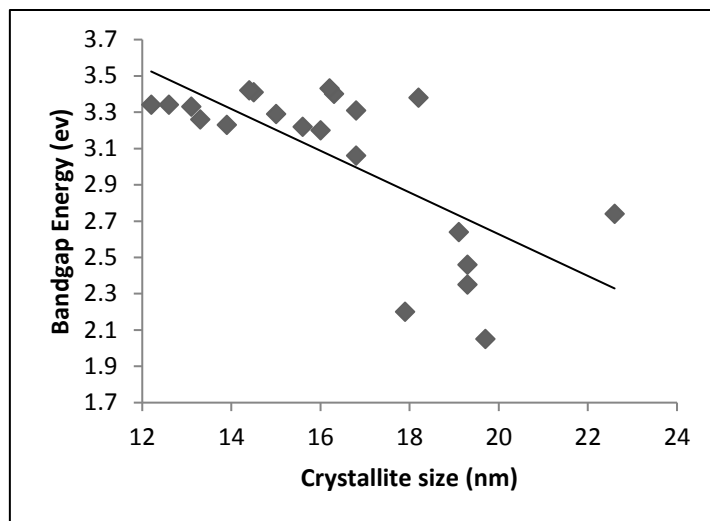


Figure 52
Correlation between crystallite size and
energy bandgap from literature

Similar correlation between the crystallite size and band gap energy can be obtained from literature, see Table 7 and Figure 52; the bandgap energy decreases when the crystallite size increases. All the chosen research papers used the same method, sol-gel dip coating, for the preparation of films, except the last, which used doctor blade method. However, for our results, there is no direct relation between bandgap energy and roughness.

4.5 Photo-Degradation Measurements

In order to compare pure TiO_2 and M-Nd co-doped TiO_2 catalytic efficiency, Rhodamine B (RhB) dye has been used as a photo-catalytic indicator. Fig. 53 shows the absorbance spectra of M-Nd TiO_2 thin films at different exposure times in the wavelength range of 500–750 nm.

The percentage of photo-degradation (D) of RhB solutions in Fig. 58 was evaluated by the following equation: (6)

$$D = \frac{C_0 - C_t}{C_0} \times 100 \quad (6)$$

where C_0 and C_t are the reactant concentrations at $t = 0$ and at time t .

The photo-catalytic reaction rate constant (k) can be calculated by re-plotting the photo-degradation ratio of according to the following pseudo-first order reaction equation (7):

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app}t \quad (7)$$

where C_0 and C_t are the absorbance maxima of the RhB dye before and after irradiation time, respectively.

.

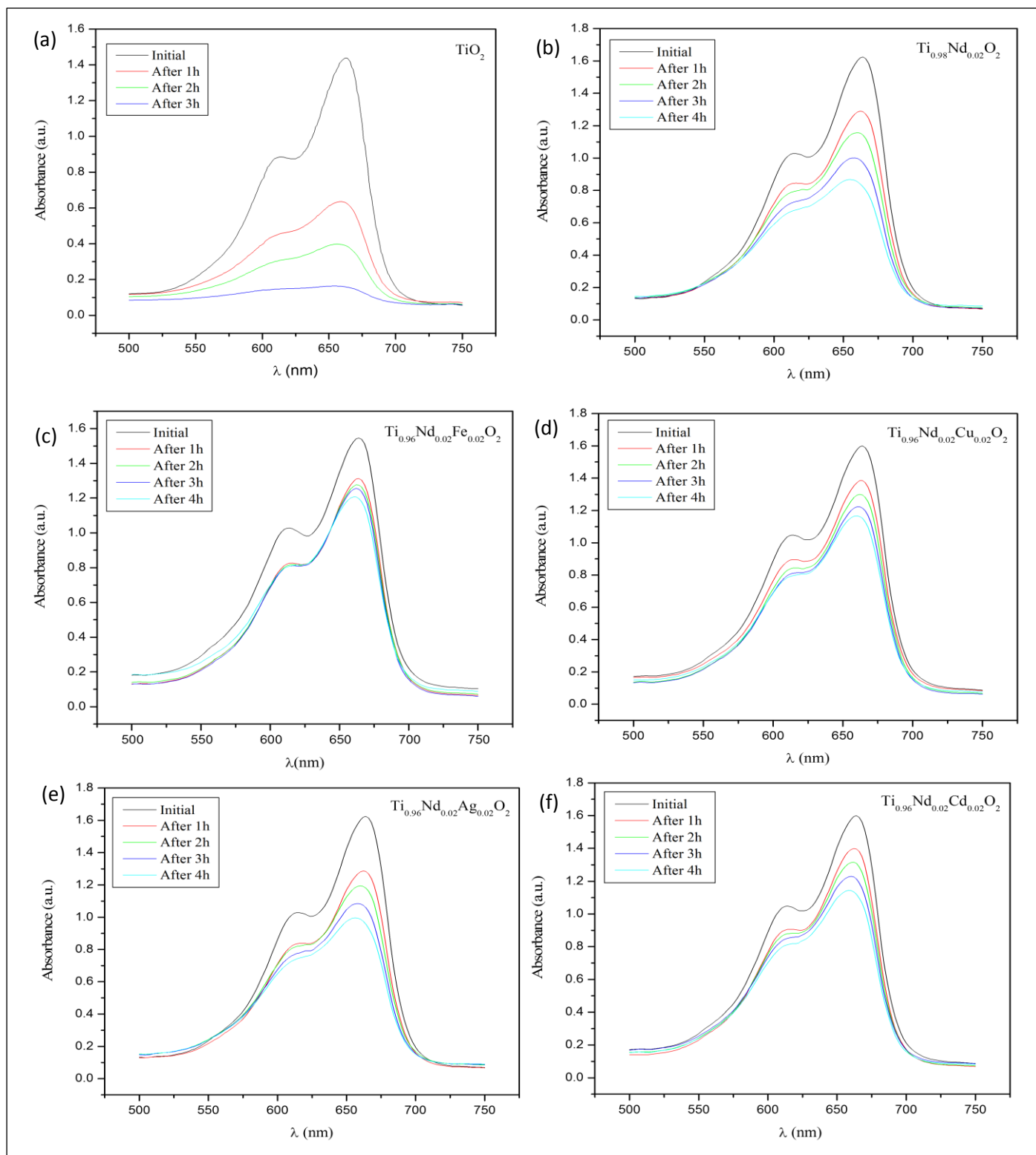


Figure 53

Optical absorption spectra of the Rhodamin B dye measured after the photocatalysis process for different exposure times. (a) Pure TiO_2 , (b) Nd-TiO_2 (c) $(\text{Nd,Fe})\text{-TiO}_2$ (d) $(\text{Nd,Cu})\text{-TiO}_2$ (e) $(\text{Nd,Ag})\text{-TiO}_2$ (f) $(\text{Nd,Cd})\text{-TiO}_2$

Fig. 55 shows the photo-catalytic decomposition of RhB dye in aqueous solution by pure and Nd-M-doped TiO_2 thin films under UV light irradiation. The photocatalytic removal efficiency of pure TiO_2 thin film reaches about 75% of initial RhB concentration after 3h, while this percentage decreases extremely; only 45% of removal efficiency is observed for Nd-doped TiO_2 films. On the other hand, the degradation decreases more with co-doped TiO_2 thin films; the percentages are about 38%, 29%, 28% and 20% for Ag, Cd, Cu and Fe co-doped Nd- TiO_2 respectively. The as-obtained low efficiencies may be attributed to several factors: (i) Crystallite size, since the surface area increases with decreasing the crystallite size; (ii) Surface roughness, whereas the roughness affect the light interaction with the surface; (iii); Band gap energy is very important for the photocatalyst (as displayed in chapter 1); and (iv) doping concentration, with high concentration the doped elements covers the surface and form e-h pairs that needs photons for recombination as shown in Figure 54 (Bensouici, F. et al., 2015).

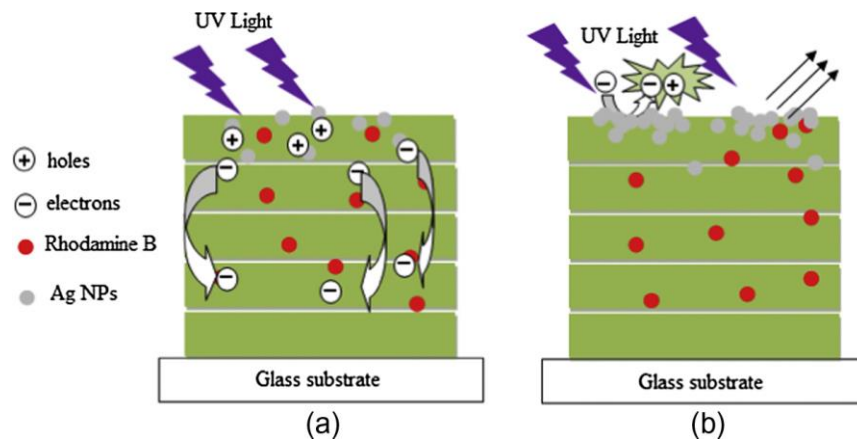


Figure 54

Schematic representation of cross sections of TiO_2 thin films doped (a) with low Ag NPs concentration and (b) with too high Ag NPs concentration (Bensouici, F. et al., 2015)

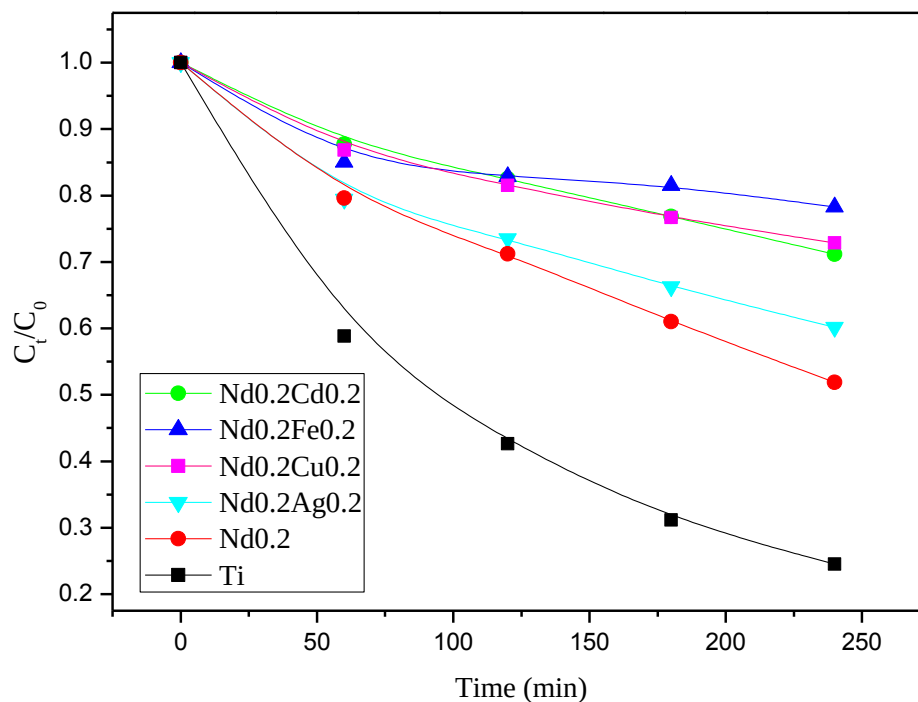


Figure 55

Degradation of Rhodamine B dye as function of the UV-light exposure time

As shown in Figure. 56 and Figure 57, the reaction constant k value decrease with doping from 0.00631 min^{-1} for TiO_2 to 0.00118 min^{-1} for Nd-Fe co-doped TiO_2 thin films. While the in-between k values are equal to 0.00279 , 0.00228 , 0.00145 and 0.00148 min^{-1} for Nd doped TiO_2 and (Ag,Cu,Cd)-Nd doped TiO_2 respectively as revealed in Figure 57. This indicates that the photocatalytic reaction over pure TiO_2 occurs faster than that for co-doped Nd-M TiO_2 with UV light irradiation.

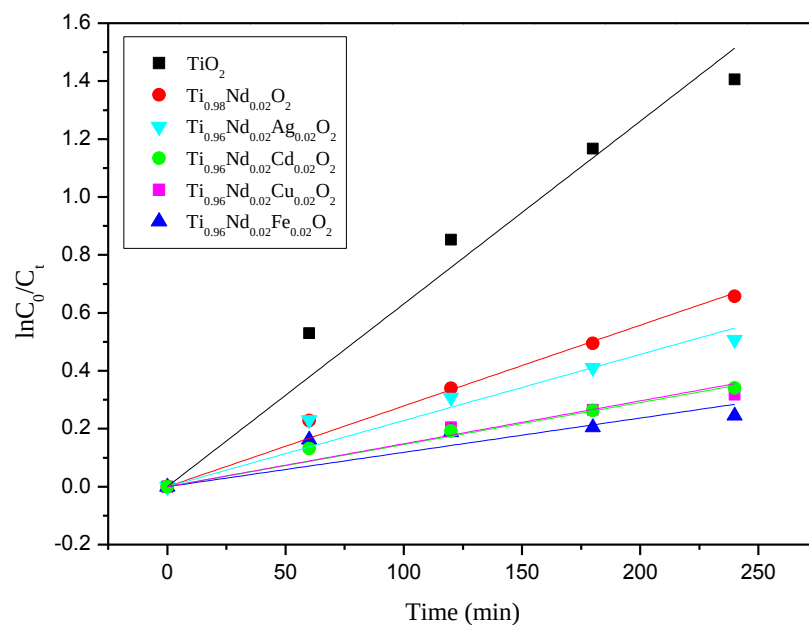


Figure 56

Corresponding plots for reaction rate constant Nd-M (Fe, Cu, Ag & Cd) doped TiO_2

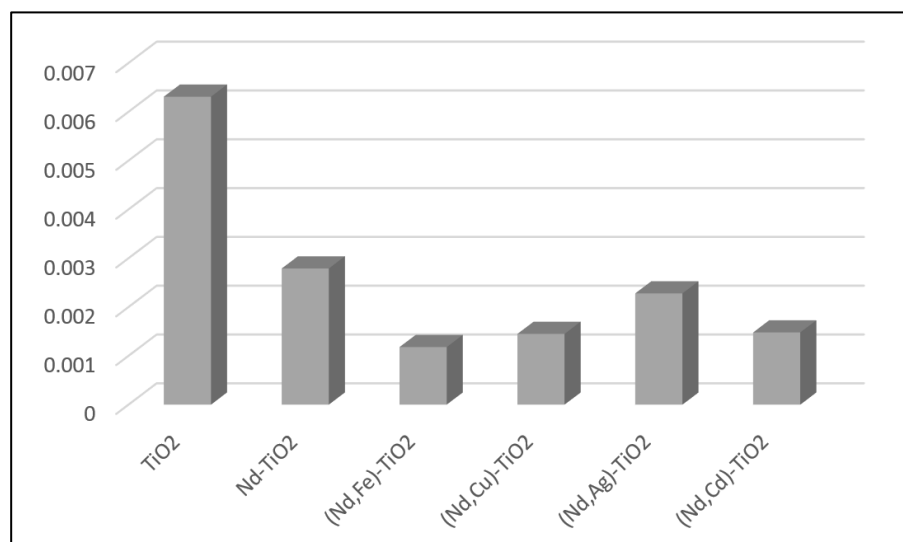


Figure 57

Histogram of variation of K_{app} as a function of different doping thin films

Table 7 also shows a comparison of the as-deposited Nd-M co-doped thin films and some selected thin films reported in the literature. It is evident that the studied system show a lower photocatalytic efficiency (PCE) rate compared to Cu doped TiO_2 system for pure TiO_2 sample. However, comparing single doped TiO_2 with co-doping system, the co-doped TiO_2 is higher than single doping, that is with Ag doped TiO_2 system compared with Co-doped system for the same content of Ag doping. This is noticed in all systems, but the dye, which was used for other systems, is different and that affect the degradation rate as shown in Cd doped system.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

5.2 Research Study's Recommendations and Suggestions

5.1 Conclusion

TiO₂ thin films doped with Nd and co-doped with Nd-M (Fe, Cu, Ag and Cd) are deposited onto glass substrate by simple wet chemical route. It is found that with both Nd-M co-doping, the photocatalytic activity is not enhanced compared to pure TiO₂, which is attributed to several factors such as crystallite size, surface roughness, band gap energy, and doping concentration. The lattice parameters almost remained same for all films because the doping elements may form nanoclusters onto TiO₂ layer surface; the doped elements do not dissolve into TiO₂ crystal lattice. The surface roughness increases with increasing the crystallite size. The band gap energy calculated by two different methods is found to be slightly higher when measured by Uv-vis spectroscopy compared to photoluminescence. Uv-vis spectroscopy shows good correlation between the energy band gap and the crystallite size. From photoluminescence, Nd doped TiO₂ thin film has the highest band gap energy, while (Nd, Fe) co-doped TiO₂ has the lowest band gap energy.

5.2 Research Study's Recommendations and Suggestions

For future research, we recommend performing tests on other dyes such as Methyl Orang, Methylene Blue, Methyl Red, etc. Also, we propose to synthesize new co-doped rare earth (RE) like Eu, Er, etc and transition metal (TM) like Ni, Co, etc with TiO₂ thin films. We suggest also testing different doping concentrations for both transition metals and rare earth. Finally, we suggest performing tests on flow water and using different designs of the microreactor to be as zigzag shape or vertical in the pipes by the help of the research team from Chemical Engineering, et the University of Bahrain.

References

- Andronic, L., Enesca, A., Vladuta, C., & Duta, A. (2009). Photocatalytic activity of cadmium doped TiO₂ films for photocatalytic degradation of dyes. *Chemical Engineering Journal*, 152(1), 64-71.
- Bensouici, F., Souier, T., Iratni, A., Dakhel, A., Tala-Ighil, R. and Bououdina, M. (2014). Effect of acid nature in the starting solution on surface and photocatalytic properties of TiO₂ thin films. *Surface and Coatings Technology*, 251, pp.170-176.
- Bensouici, F., Souier, T., Dakhel, A., Iratni, A., Tala-Ighil, R., & Bououdina, M. (2015). Synthesis, characterization and photocatalytic behavior of Ag doped TiO₂ thin film. *Superlattices And Microstructures*, 85, 255-265.
- Bensouici, F., Bououdina, M., Dakhel, A., Tala-Ighil, R., Tounane, M., & Iratni, A. et al. (2017). Optical, structural and photocatalysis properties of Cu-doped TiO₂ thin films. *Applied Surface Science*, 395, 110-116.
- Bokare, A., Pai, M. & A. Athawale, A. (2013). Surface Modified Nd Doped TiO₂ Nanoparticles as Photocatalysts In UV And Solar Light Irradiation. *Solar Energy*, 91, 111-119.
- Diamond, S., Kennedy, A., Melby, N., Moser, R., Poda, A., Weiss, C. and Brame, J. (2017). Assessment of the potential hazard of nano-scale TiO₂ in photocatalytic cement: application of a tiered assessment framework. *NanoImpact*, 8, pp.11-19.
- Differencebetween.net. (2017). *Differences Between Rutile and Anatase Titanium Dioxide | Difference Between*. [online] Available at:
<http://www.differencebetween.net/science/chemistry-science/differences-between-rutile-and-anatase-titanium-dioxide/> [Accessed 23 Aug. 2017].
- Ennaceri, H., Boujnah, M., Taleb, A., Khaldoun, A., Sáez-Araoz, R., Ennaoui, A., El Kenz, A. and Benyoussef, A. (2017). Thickness effect on the optical properties of TiO₂ - anatase thin films prepared by ultrasonic spray pyrolysis: Experimental and ab initio study. *International Journal of Hydrogen Energy*, 42(30), pp.19467-19480.

Golubović, A., Šćepanović, M., Kremenović, A., Aškračić, S., Berec, V., Dohčević-Mitrović, Z. and Popović, Z. (2008). Raman study of the variation in anatase structure of TiO₂ nanopowders due to the changes of sol–gel synthesis conditions. *Journal of Sol-Gel Science and Technology*, 49(3), pp.311-319.

Haider, Adawiya J. et al. "Exploring Potential Environmental Applications of TiO₂ Nanoparticles." *Energy Procedia* 119 (2017): 332-345.

Kandiel, T., Ahmed, A. and Bahnemann, D. (2016). TiO₂ (B)/anatase heterostructure nanofibers decorated with anatase nanoparticles as efficient photocatalysts for methanol oxidation. *Journal of Molecular Catalysis A: Chemical*, 425, pp.55-60.

Mangrola, M. and Joshi, V. (2017). Synthesis, Characterization and Study of Influence of Pure TiO₂ Nanoparticles Thin Film Developed By e-Beam Evaporation. *Materials Today: Proceedings*, 4(2), pp.3832-3841.

Miller, M. and Wang, J. (2015). Coupled effects of deposition and annealing temperatures on optical, electrical and mechanical properties of titanium oxide thin films. *Vacuum*, 120, pp.155-161.

Ned.ipac.caltech.edu. (2017). *Interaction of Nanoparticles with Radiation - A. Li*. [online] Available at: <https://ned.ipac.caltech.edu/level5/Sept03/Li/Li4.html> [Accessed 27 Aug. 2017].

Reyes-Coronado, D., Rodríguez-Gattorno, G., Espinosa-Pesqueira, M., Cab, C., de Coss, R. and Oskam, G. (2008). Phase-pure TiO₂ nanoparticles: anatase, brookite and rutile. *Nanotechnology*, 19(14), p.145605.

Rigaku.com. (2017). *Multipurpose X-ray diffraction system | Rigaku*. [online] Available at: <http://www.rigaku.com/products/xrd/ultima> [Accessed 23 Aug. 2017].

Tang, W., Chen, X., Xia, J., Gong, J., & Zeng, X. (2014). Preparation of an Fe-doped visible-light-response TiO₂ film electrode and its photoelectrocatalytic activity. *Materials Science and Engineering- B*, 187, 39-45.

Zongyan, Zhao et al. "Effects of Nonmetal Doping On Electronic Structures and Optical Property of Anatase TiO₂ from First-Principles Calculations." *Rare Metal Materials and Engineering* 44.7 (2015): 1568-1574. Web.

الملخص

مياه الصرف الصحي الناتجة من مصادر مختلفة كالمصانع والمختبرات والصناعات الغذائية تسبب مشاكل خطيرة على البيئة. إذ يمكن أن تكون المياه الملوثة خطرة وسامة على البشر والكائنات الحية الدقيقة والحياة المائية. وقد تحتوي المياه الملوثة على مجموعة متنوعة من المواد الكيميائية مثل الأصباغ، والمعادن الثقيلة والبكتيريا. الهدف من دراستنا هو إعداد مواد جديدة ذات بنية نانوية مع خصائص محسنة ونشاط تحفيزي عالي لتكسير الأصباغ الصناعية. هذا البحث مكرس لتصنيع مفاعل صغير على أساس أفلام TiO_2 النانوية الرقيقة المطعمة تطعياً مزدوجاً للعمل على تكسير صبغة Rhodamin B (RhB) الناتجة من مختلف الصناعات في مملكة البحرين. و لقد تمت دراسة البنية، المورفولوجيا، التضاريس، الخصائص البصرية، والتكسير الضوئي لصبغة RhB باستخدام صفائح TiO_2 النقي، أو المطعم بمادة Nd، أو المطعم تطعياً مزدوجاً بمادتي (Nd,M) حيث ان M هي العناصر (Fe, Cu, Ag, Cd). هذه الصفائح تم أعدادها على هيئة طلاء بطريقة "سول جل". يوضح التحليل تكون طور التيتانيوم الامتدادي "anatase" من TiO_2 لجميع العينات. إن فحص AFM يبين تضاريس ومورفولوجيا الأفلام وتحسب "طاقة فجوة الحزمة" باستخدام طريقتين، أولاً بطريقة التآلق الضوئي، حيث ان طاقة فجوة الحزمة تتراوح بين 3.25 eV و 3.14 eV لصفائح TiO_2 المطعمة بـ Nd وشرائح TiO_2 المطعمة تطعياً مزدوجاً بـ Fe-Nd على التوالي. بالإضافة إلى ذلك، تم فحص العيوب باستخدام نفس الطريقة. فأظهرت النتائج باستخدام طريقة التحليل الطيفي في المنطقة (المرئية/ فوق بنفسجية) ان (فجوة الطاقة) تتراوح بين 3.34 eV لصفائح TiO_2 المطعمة بـ Nd و Nd-Cd و 3.23 eV لشرائح TiO_2 المطعمة تطعياً مزدوجاً بـ Nd-Ag. كما أظهر التحليل الطيفي أن نسبة تكسير الصبغة باستخدام صفائح TiO_2 تساوي 75%، وهذه الكفاءة تنخفض إلى 20% للصفائح المطعمة بـ Nd-Fe.

جامعة البحرين

قسم الفيزياء

كلية العلوم



تكسير الأصباغ عن طريق التطعيم المزدوج لصفائح ثاني أكسيد التيتانيوم النانوية

مخطط بحث لاستكمال متطلبات الحصول على درجة الماجستير في الفيزياء التطبيقية

إعداد

عالية مصطفى إسلام

20071828

إشراف

د. حسان مائع استاذ مشارك

إشراف مشارك

د. محمد بودينة استاذ مساعد

جامعة البحرين

مملكة البحرين

مايو 2018