

**Unique coating solutions for steel substrates used in
photovoltaic solar cells**

Mónica Martinho Gomes Coronha Brioso

Thesis to obtain the Master of Science Degree in
Energy Engineering and Management

Supervisor: Prof. Maria de Fátima Grilo da Costa Montemor

Examination Committee

Chairperson: Prof. Francisco Manuel da Silva Lemos

Supervisor: Prof. Maria de Fátima Grilo da Costa Montemor

Member of the Committee: Prof. Susana Paula Santos Carvalho Piçarra Gonçalves

June 2016

Acknowledgements

I am extremely grateful to all the people that made part of this journey.

Firstly, I would like to express my gratitude towards the supervisor of this thesis, Prof. Dr. Fátima Montemor for the suggestions, support, clarification of doubts and helping decide the best path to take in each step of the way.

I also would like to give my gratitude to Dr. Darya Snihirova which help me throughout this thesis. Her never-ending patience, bright ideas, explanations and support were a precious diamond along this work.

Thank you to Prof. Dr. José Figueiredo and to Prof. André Março for all the suggestions given for the state of the art and economic chapter.

I am thankful to Prof. Dr. Alda Simões for remember of giving me the Brinker book about sol-gel because it is an important tool for my thesis. Thank you for the kindness of Prof. Dr. Benilde Saramago to allow me to use the Goniometer for contact angle measurements and Diana Silva for the help any time I had measurements difficulties. I am also thankful to Dr. Ana Paula to allow me to use the UV/Vis Spectrometer and to Prof. Dr. Jorge Morgado to provide the organic solar cells and equipment to measure the efficiency. Thank you to Ricardo Oliveira for producing the organic solar cells and helping with the I-V measurements. To Bruno Fonseca for the curiosity expressed for my work, motivation to help and to provide silica nanoparticles. Thank you to Kush Upadway and Yegor Morozov for always being helpful.

In an overall point of view, the group of Corrosion Science and Surface Engineering (CSSE) from Centro de Química Estrutural (CQE) at Instituto Superior Técnico (IST) is formed by amazing people and a work environment like this is rare to find. So, it was an honour to work this few months along enthusiastic researchers. I am thankful to all the lunches spend together with the group. A great attitude creates a great person and without the spirit of the elements of this group, this journey had been much more difficult.

A special thanks to my parents, Joaquim and Paula Brioso, for all the strength and support given. After ups and downs along the way, I always can count on you. My grandmother Madalena Gomes for always being worried about me, like only grandmothers know. Thank you to my cousin Mafalda Vilhais to be always a great companionship and Jorge Andrade for being supportive.

I am also grateful to my friends, Daniela Marum, Cristiana Costa, Joana Antunes, Paulo Meyrelles, Diogo Gonçalves, Rodolfo Matos, André Cunha and Tânia Santos to turn my days brighter.

Abstract

Maintenance of photovoltaic solar panels is hardworking and expensive even because the large-scale solar plants are often sited faraway from water sources, e.g. deserts where dust particles accumulation on panels surface leads to a decrease in efficiency.

The aim of this MSc work is to develop a unique coating compatible with glass in PV solar cells surface and steel used in the structure support. The superhydrophobic coating is intended to be water and dust repellent and was prepared through the sol-gel route using different organosilanes as precursors. Contact angles were obtained by the Sessile Drop method. Hexamethyldisilazane (HMDS) and Trimethylethoxysilane (TMES) precursors achieved superhydrophobicity and Trimethoxy(octyl)silane (TMOOS) almost.

The novel coating was composed with a molar ratio of ammonium hydroxide (2M NH₄OH) as catalyst, TMES precursor and ethanol solvent with 3.78:1:5.78, respectively. A superhydrophobic coating compatible with the previous substrates achieved contact angles above 155°. Self-cleaning properties were also visualized without sliding angle.

The coating was applied by spray and dip-coating techniques on glass slides, steel and PV solar cells and characterized through Optical microscopy(OM) and Scanning Electron Microscopy (SEM) to ensure a transparent and well distributed coating. The coating with TMES sol-gel without and with modification of silica nanoparticles presented a percentage of transmission of 100% (antireflective) and 91%, respectively. Efficiency was evaluated in organic solar cells and decreased 0.244% in the TMES sol-gel coating and 0.354% in the modified sol-gel coating.

Therefore, the goals were achieved and the developed coating is inexpensive, simple to fabricate, of easy application and a promising viable alternative to existing solutions.

Keywords: Sol-gel, organosilanes, superhydrophobic, self-cleaning, solar cells, functional coatings.

Resumo

Nesta dissertação obteve-se um revestimento que elimina os elevados custos de manutenção dos painéis solares fotovoltaicos. Devido à acumulação de sujidade na superfície dos painéis a sua eficiência diminui. A produção de um revestimento superhidrofóbico com propriedades auto-limpantes mantém a sua superfície limpa. É único, porque é compatível com o vidro das células solares e com o aço da estrutura dos painéis. O revestimento obtido é simples de produzir, tem baixos custos e é fácil de aplicar.

Este foi produzido por sol-gel e aplicado em substratos de aço, lâminas de vidro, painel solar comercial e células solares orgânicas. Foram usados organosilanos como precursores e variadas as condições. A superhidrofobicidade foi atingida com Trimetiletoxissilano (TMES), Hexametildissilazano (HMDS) e quase com Trimetoxi(octil)silano (TMOOS).

O melhor revestimento obtido é composto por: 2M NH₄OH: TMES: EtOH com o rácio molar 3.78:1:5.78, respetivamente e foram obtidos ângulos de contacto superiores a 155° e observadas propriedades auto-limpantes sem inclinar o substrato. A aplicação do revestimento foi feita por spray e imersão.

A caracterização foi feita por comparação entre o revestimento com TMES sol-gel e o TMES sol-gel modificado com nanopartículas de sílica. Utilizou-se o método de gota Sessile, microscopia óptica e microscopia electrónica de varrimento (MEV). No substrato com o revestimento feito com TMES sol-gel observou-se uma estrutura fina e transparente, através do espectrofotómetro UV/Vis foi analisada a percentagem de transmissão(%T) que foi anti-reflexiva e a eficiência diminui 0.244% após aplicado em células orgânicas. Enquanto que no revestimento com TMES sol-gel modificado são visualizadas aglomerações, a percentagem de transmissão foi de 91 % e a eficiência diminui 0.354%.

Palavras-chave: Sol-gel, organosilanos, superhidrofóbico, auto-limpante, células solares, revestimentos funcionais.

Table of contents

List of Figures	vii
List of Tables	ix
List of Abbreviations.....	x
List of Symbols	xii
1. Introduction.....	1
1.1 Photovoltaic solar energy maintenance problem	1
1.2 Aims of the thesis	2
1.3 Motivation.....	2
1.4 Thesis outline	3
2. State of the art	6
2.1 Photovoltaic solar energy.....	6
2.1.1 The largest energy resource	6
2.1.2. Solar cells development- PV history and Market	7
2.1.3. Types of solar cells.....	10
2.1.4. Photovoltaic systems – PV and CPV	12
2.1.5. Overview into PV solar energy sustainability.....	14
2.2 Maintenance of solar panels	15
2.2.1 Access and availability.....	15
2.2.2 Cleaning Frequency	16
2.2.3. Types of cleaning processes	17
2.3 Unique coating with self-cleaning properties.....	20
2.3.1. Superhydrophobic coating with self-cleaning properties	21
2.3.2. Energy applications and benefit properties of superhydrophobic coatings	28
3. Experimental methods.....	29
3.1 Sol-gel route.....	29
3.1.1. Precursors.....	29
3.1.2. Catalyst, solvent, pH and H ₂ O:Si molar ratio (r') dependence	30
3.1.3. Hydrolysis and condensation	31
3.1.4. Silica Nanoparticles Modification	33
3.1.5. Substrates preparation and coating application.....	33
3.1.6. Dip-coating.....	35
3.1.7. Spray coating	35
3.1.8. Curing	36
3.2. Characterization techniques.....	36
3.2.1. Contact angle measurements	37
3.2.2. Optical microscope	38

3.2.3. Scanning Electron Microscope (SEM).....	38
3.2.4 Transmittance measurements	39
3.2.5. Solar cells efficiency evaluation	40
4. Results and discussion.....	42
4.1. Overview of the experimental results	42
4.2. Experimental Setup	43
4.3. Contact angle measurements assessment.....	45
4.3.1. Coating with TMOOS precursor.....	45
4.3.2. Coating with HMDS precursor	46
4.3.3. Coating with TMES precursor and pH influence on contact angles.....	47
4.2.4. Comparison between coatings and selection of the best one	48
4.3.5. Comparison between different substrates and coating applications.....	49
4.3.6. Final coating conditions and results	52
4.4. Optical and Scanning Electron microscopy characterization.....	52
4.5. Transmittance measurements.....	57
4.6. Solar cells efficiency evaluation	58
4.7. General discussion of the experimental results	59
5. Economic Methodology and Assessment – the use of coatings instead of manual maintenance in PV solar panels.....	62
5.1. Viability study from the investor perspective (energy producer)	62
5.1.1. Which sells energy to the distributors.....	62
5.1.2. Physical investment is done in PV solar panels already installed which implies a financial value of €/m ²	62
5.1.3. Implies a reduction in maintenance cost	63
5.1.4. Implies annual average efficiency increment from the panel.....	63
5.2. Case Study of Martifer Solar Algarve Projects.....	66
5.2.1. Characteristics of the PV solar plant	66
5.2.2. Coating Characteristics.....	67
5.2.3. Saving Costs in O&M	67
5.2.4. Increments in Energy Production	68
5.2.5. Final Remarks.....	69
6. Conclusions	70
7. Outlook and Future perspectives.....	72
References	73

List of Figures

Figure 1 - Annual renewable and non-renewable energy quantities produced and potential generation comparing with world energy requirement and the solar radiation supplied [13].	6
Figure 2 – Representation of a simple solar cell when operating [18].	7
Figure 3 - Schematics from solar cells structure: 1- single crystalline silicon solar cell [28]; 2- polycrystalline silicon solar cell[29]; 3- Amorphous silicon solar cell [30]; 4 - copper indium gallium di-selenide (CIGS) solar cell [18]; 5- cadmium telluride solar(CdTe) solar cell [18]; 6 - dye-sensitized(DSSC) solar cell [18]; 7-organic solar cell [31];	11
Figure 4 - Schematic of the PV solar panels disposal [32].	12
Figure 5 - Main CPV technologies [24]. Adapted from International Energy Agency(IEA).	13
Figure 6 - Annual average solar irradiance (kWh/m ²) distribution around the world [12].	15
Figure 7 - Schematic representation of the self-cleaning mechanisms when the surfaces are tilted to a certain degree, denoted as inclination angle (θ_i). On the left is presented a superhydrophilic surface where the water goes beneath the contaminant and on the right is presented a superhydrophobic surface where water picks up the contaminant (Adapted from [46]).	21
Figure 8 - Three phases in mutual contact defined by various interfacial tensions ruled by Young's equation [47].	22
Figure 9 - Schematic with the representation of a hydrophilic, hydrophobic and ultra-hydrophobic surfaces (Adapted from [5]).	22
Figure 10 - a) Receding contact angle (θ_R) and b) Advancing contact angle (θ_A) [52].	23
Figure 11 - Schematic diagram representing the water droplets on Wenzel model (left) and Cassie-Baxter model (right) [46].	23
Figure 12 - Wetting of four different surfaces. The contact area is reduced in nanostructures surfaces and minimized in hierarchical structured surfaces [54].	25
Figure 13 - Sol stability versus pH [60, 62].	30
Figure 14 - Polymerization behaviour of aqueous silica [60, 62].	31
Figure 15 - a) Glass surface; b) carbon steel surface; c) solar panel surface [65] and d) glass encapsulated organic solar cell (OPV) only used for efficiency evaluation.	34
Figure 16 - Steps of dip-coating technique: a) immersion; b) ascending; c) deposition; d) drainage; e) evaporation, adapted from [60].	35
Figure 17 - Equipment used for dip-coating (Siemens Logo! 12/24RC model).	35
Figure 18 - Goniometer used for the wettability measurements.	37
Figure 19 - Schematic of a superhydrophobic coating (CA>150°) with self-cleaning properties (sliding angle and contact angle hysteresis (CAH) lower than 10°) [8].	37
Figure 20 - Scheme of the scanning electron microscope components (a)) [70] and the equipment used (b)).	39
Figure 21 - UV/Vis Spectrometer (PerkinElmer, Lambda 35).	39
Figure 22 - Typical J-V curve for a solar cell (Adapted from [72]).	40
Figure 23 - Structure and picture of the organic solar cell used.	41
Figure 24 - a) Measurement cell; b) Set-up from the equipment used for measurement of electrical characteristics; c) Solar simulator.	41
Figure 25 - Contact angles in both steel and glass substrates with different percentages (%) of TMOOS (TMOOS: TEOS molar ratios).	45
Figure 26 - Contact angle measurements with different HMDS:TEOS molar ratios and with HMDS sol-gel unmodified and modified with 1 wt. % of silica nanoparticles.	46
Figure 27 - pH influence on the contact angles. Variation of %TMES and application on glass substrates.	47
Figure 28 - Comparison of the contact angles in the glass substrate and using different silanes. (a) with the addition of SiO ₂ nanoparticles and (b) without the addition of SiO ₂ nanoparticles.	49

Figure 29 - Contact angles from the TMES sol-gel coating with and without SiO ₂ by spray (a) and dip-coating (b) application to both glass and steel substrates.	50
Figure 30 - Contact angles with TMES sol-gel without and with addition of silica nanoparticles obtained in the solar panel surface through spray coating (3x and 1x sprayed) and dip-coating techniques.	49
Figure 31 - Self-cleaning observation (SA<10°) through multiple shots taken by a digital camera while measuring the static contact angles in the goniometer with the different substrates.	51
Figure 32 - Coated glass substrate (through dip-coating) with TMES sol-gel and HV=20 kV for SEM. a) SEM micrograph with scale=100µm and mag= 100x; b) SEM micrograph with scale=1µm and mag=4000x; c) OM picture with scale=100µm and mag=20x; d) OM picture with scale=200µm and mag=10x.....	53
Figure 33 - Coated glass substrate (through dip-coating) with TMES sol-gel modified with silica nanoparticles and HV=20kV. a) SEM micrograph with scale=10 µm and mag=1000x; b) SEM micrograph with scale=1µm and mag=11,000x; c) OM picture with scale=100 µm and mag=20x; d) OM picture with scale=50 µm and mag=50x.	53
Figure 34 - SEM micrographs (HV=20 kV) of the coated glass substrate (dropwise application) with TMES sol-gel modified with silica nanoparticles: a) scale=100 µm and mag=100x; b) scale=10µm and mag=430x; c) scale=10 µm and mag=950x; d) scale=10 µm and mag=1500x.	54
Figure 35 - SEM micrographs (HV=20 kV) of the coated steel substrate (dip-coating application) with TMES sol-gel: a) scale=10 µm and mag=1000x; b) scale=1µm and mag=5000x. TMES sol-gel modified with silica nanoparticles: c) scale=10 µm and mag=1000x; d) scale=1µm and mag=5000x..	55
Figure 36 - Solar panel coated with a), b), c) TMES sol-gel and d), e), f) TMES sol-gel modified with silica nanoparticles. SEM micrographs with HV=15 kV: a) scale=10µm and mag=1000x; b) scale=1µm and mag=5000 µm; c) scale=100 nm and mag=35,000x; d) scale=10µm and mag=1000x; e) scale=1µm and mag=5000 µm; f) scale=1µm and mag=13,000 µm.	56
Figure 37 - Energy Dispersive Spectrum (EDS) from the coated solar panel with TMES sol-gel. Spectrum 1 formation and surroundings – Spectrum 2 – are shown on Figure 35 c).	57
Figure 38 - Optical transmission spectra for glass samples with TMES sol-gel coating and TMES sol-gel coating modified with silica nanoparticles (SNPs).....	57
Figure 39 - J-V curves. Organic cell 1 - comparison between uncoated and coated surface with TMES sol-gel coating; Organic cell 2 - comparison between uncoated surface and surface with TMES sol-gel coating modified with silica nanoparticles.....	59
Figure 40 - Average monthly global irradiation over the horizontal and the fixed plan with 30° and 60°, in Lisbon (Adapted from [17]).....	64
Figure 41 - Average monthly global irradiation with and without coating in a titled fix plan with 30° in Lisbon (adapted from [17]): a) with Portugal climate; b) if Portugal had an arid climate.	65
Figure 42 - Avalades, Silves PV plant (left) and Ferreiras, Albufeira PV plant (right) [80].	66

List of Tables

Table 1 - Main countries producers in 2009 and the respective annual production of PV cells and modules (MW) (Adapted from [19]).....	8
Table 2 - Main companies producers in 2009 (Adapted from [19]).	8
Table 3 - Technology Innovation System (TIS) components for China. Each component promotes the PV technology development, adapted from (Adapted from [21]).....	9
Table 4 - Types of solar cells and respective efficiency, market share, PV module size and output power (Adapted from [24]).....	10
Table 5 - Overall advantages and disadvantages on PV solar systems (Adapted from [24]).	13
Table 6 - Reported values of EPBT, GHG emission rates and primary energy requirements of different types of solar cells (Adapted from [34]).....	14
Table 7 - Advantages and disadvantages of different cleaning methods for dust removal from PV module surfaces (Adapted from [1])......	19
Table 8 - Overview of biomimetic self-cleaning surfaces present in nature (Adapted from [46, 53, 54]).	25
Table 9 - Summary of methods to fabricate superhydrophobic coatings from various materials (Adapted from [5]).	27
Table 10 - The precursors used in the experimental work were: TEOS(98%), TMES(98%), HMDS(99%), TMOOS(96%), TMOOS(96%), TMOOS(96%), TMOOS(96%), GPTMS(98%), APTES(99%) and APTMS(97%). All the silanes were purchased from Sigma-Aldrich.	29
Table 11 - Solvents and catalysts used.	31
Table 12 - Mechanisms of hydrolysis [60].....	32
Table 13 - Mechanisms of condensation [64].	32
Table 14 General characteristics and physical-chemical properties from WACKER(HDK®2000) silica nanoparticles.	33
Table 15 - Solar panel characteristics [65].....	34
Table 16 - A glance table from the experimental work.	44
Table 17 - Contact angles of the uncoated substrates.	45
Table 18 - Different molar ratios used between TMOOS:TEOS.	46
Table 19 - Contact angle measurements through Sessile Drop Method of TMES sol-gel coating modified with silica nanoparticles when the pH=6.5.	48
Table 20 - Molar ratios applied for the three precursors attempts.	48
Table 21 - Best contact angles achieved with TMES sol-gel coating modified with silica nanoparticles in glass, steel and PV solar panel surface.	51
Table 22 - Formulation, conditions and contact angle measurements from the best coating achieved.	52
Table 23 - Organic cells performance parameters: J_{sc} , V_{oc} , P_{max} , FF and η with uncoated and coated surface.....	58

List of Abbreviations

AC	Alternating Current
ADSA	Axisymmetric Drop Shape Analysis
Al	Aluminium
APTES	(3-aminopropyl)triethoxysilane
APTMS	(3-aminopropyl)trimethoxysilane
a-Si	Amorphous silicon
Au	Gold
BIPV	Building Integrated Photovoltaics
CA	Contact angle
CAH	Contact Angle Hysteresis
CdTe	Cadmium Telluride Cells
CIGS	Copper Indium Gallium Selenide
CIS	Copper Indium Selenide
CO ₂	Carbon dioxide
CPV	Concentrated Photovoltaic
c-Si	Crystalline silica
CSP	Concentrated Solar Power
Cu	Copper
DC	Direct Current
DL	Decree Law
DMF	Dimethylformamide
DNI	Direct Normal Irradiance
DSSCs	Dye-sensitized solar cells
EDS	Electrodynamic Screens
EDS	Energy Dispersive Spectrometer
EIS	Electrochemical Impedance Spectroscopy
EPBT	Energy Payback Time
EtOH	Ethanol
F8T2	Poly[[2,2'-bithiophene]-5,5'-diyl(9,9-dioctyl-9H-fluorene-2,7-diyl)]
FEG-SEM	Field Emission Gun Scanning Electron Microscopy
FF	Fill Factor
GHG	Greenhouse gases
GPTMS	(3-Glycidyloxypropyl)trimethoxysilane
HMDS	Hexamethyldisilazane
IC	Investment Cost
IEA	International Energy Agency
i-prop	Isopropanol
ITO	Indium Tin Oxide
LCA	Live Cycle Assessment
LFR	Linear Fresnel Reflector
LiF	Lithium fluoride
MENA	Middle East and North Africa
MeOH	Methanol
MTES	Methyltriethoxysilane
NASA	National Aeronautics and Space Administration

NH ₄ OH	Ammonium Hydroxide
NOCT	Nominal Operating Cell Temperature
O&M	Operation and Maintenance
OM	Optical Microscope
OPEX	Operational expenditures
PCBM	Phenyl-C61-butyric acid methyl ester
pc-Si	Polycrystalline Silica
PDMS	Polydimethylsiloxane
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PS	Polystyrene
PV	Photovoltaic
R&D	Research and Development
RH	Relative humidity
RT	Room Temperature
SEM	Scanning Electron Microscopy
Si	Silane
SiO ₂	Silicon dioxide or silica
S _{N2}	Nucleophilic Substitution Reactions
SNPs	Silica Nanoparticles
STC	Standard Test Conditions
TEOS	Tetraethylorthosilicate or tetraethoxysilane
TiO ₂	Titanium dioxide or titania
TIS	Technology Innovation System
TMES	Trimethylethoxysilane
TMODS	Trimethoxy(octadecyl)silane
TMOOS	Trimethoxy(octyl)silane
TMOS	Tetramethoxysilane
WCA	Water Contact Angle
ZnO	Zinc Oxide

List of Symbols

❖ Greek Symbols

- θ_A – Advancing contact angle;
 θ_C – Cassie- Baxter contact angle;
 θ_i – Inclination angle;
 θ_R – Receding contact angle;
 σ_{lg} – Tension between interfacial liquid-gas;
 σ_{sg} – Tension between interfacial solid-gas;
 σ_{sl} – Tension between interfacial solid-liquid;
 θ – Water contact angle;
 θ_w – Wenzel contact angle;
 λ – Wavelength;

❖ Latin Symbols

- f_s – Area fraction of the solid on the surface;
 f_v – Area fraction of the vapour on the surface;
 P_{max} – Maximum power;
 V_{oc} – Open circuit voltage;
 I_{sc} – Short-circuit current;
 r – Surface roughness factor;
 I_{mp} – maximum charging power;
 r' - H₂O:Si molar ratio
 η – Efficiency;
 J - Current density;
 J_{sc} - Short-circuit current density;
 A – Absorbance;
 T - Transmittance;
 V_m – Maximum Voltage;

1. Introduction

1.1 Photovoltaic solar energy maintenance problem

In the current days, the demand for photovoltaic (PV) solar cells is increasing and for that reason the research in this field has been raising too. Maintenance of photovoltaic solar panels is a major concern to be possible to maintain the efficiency of the energy production. The drawback of this operation is the increase of operational expenditures (OPEX).

Most of the large-scale photovoltaic solar installations are located in remote places with difficult access or in regions with lack of water. Seven of the world deserts are located between 35°N to 35°S and within these latitudes is received the highest direct normal irradiance (DNI). These deserts can fulfill the globally energy needs with solar power technologies, including photovoltaic (PV), concentrated photovoltaic (CPV) and concentrated solar power (CSP) systems. Middle East, Australia, U.S.A, China and Europe is where is concentrated the biggest amount of PV technologies in the whole world [1, 2].

Sand dust particles deposition (e.g. Mojave Desert in Southwestern United States and Negev Desert in Southern Israel), mud deposition in deserts with high percentage of humidity created by nearby water sources (e.g. Brazilian Northeastern Caatinga and Sebkhah Tah in Western Sahara Desert) and pollution particles deposition (e.g. China), are the main causes of dirtiness in the panels surface. These effects are translated into a decrease of about 40% in solar power conversion for each 4 gram of dust per square meter [1, 2]. The solar panels can lose incident light through reflection by the cover glass and mainly through scattering or absorption by particulates on the solar panels decreasing its power conversion efficiency [3]. Efficiency loss due to panel dirt can also be problematic in areas more rarely visited, such as unmanned lighthouses and observatories. There is the need of regular maintenance in order to maintain the efficiency and the overall performance of the PV solar panels [4]. Cleaning of solar panels from contaminants to maintain the optimum solar harvesting capabilities is time consuming and expensive [5]. There are locations where the photovoltaic solar panels are not maintained at all. For this reason, lower amounts of electricity are produced and the initial investments are not fully recovered during the panels lifetime. To avoid this problem, and to boost the market of renewable energies, there is an urgent need of solutions to improve the efficiency of PV solar panels exposed to dusty and polluted atmospheres.

Since the last decade, self-cleaning coatings have attracted attention in the scientific community and industry exploitation. These coatings have been made artificially by mimic biological surfaces, such as lotus leaf, gecko, namib desert beetle and water striders [6]. Some of the self-cleaning coatings applications are: textile industry (self-cleaning clothing), automobile industry (self-cleaning windshield glass, car bodies and mirrors), optical industry (cameras, sensors, lenses and telescopes), aerospace industry (non sticky surfaces), windows (window coatings), paints (exterior paints with self-cleaning properties), etc. [5].

In the last years, a cost-effective solution to the photovoltaic solar panels maintenance was claimed by applying a superhydrophobic coating with self-cleaning properties in solar cells. This solution is based in the superhydrophobic principle widely known as “Lotus effect” that enables to create a self-cleaning surface. Superhydrophobicity makes the water repellent and the self-cleaning property prevents dirt from forming an intimate contact with the surface. Consequently, as the water droplets roll onto the surface, they carry along the contaminants [3].

Multiple advantages can be achieved by using superhydrophobic coatings with self-cleaning properties in solar cells. The advantages include: effectively avoids the blocking of sunlight and the induced efficiency reduction due to dust accumulation, no requirement for water as maintenance procedure, easy to apply, decreased cost and since the lifetime of the coating can be of several years, this allows to have a lower cleaning frequency in comparison to other types of cleaning maintenance, such as manual maintenance [7, 8].

In order to design and to produce such coating it is necessary to formulate a superhydrophobic sol-gel. Sol-gel coatings can be applied on a variety of substrates and by controlling the surface morphology and chemical composition, it is possible to achieve an optimum combination of surface roughness and superhydrophobic functionality, which can result in most effective self-cleaning properties [9, 10]. Chemical compositions determine the surface free energy and thus have a great influence on wettability [7]. Silica (SiO_2) can also be used as an additive in the sol-gel to improve the superhydrophobic characteristics and the mechanical properties [11].

1.2 Aims of the thesis

This MSc thesis has the purpose of producing a superhydrophobic coating through sol-gel route to apply in photovoltaic solar cells. The functional coating must be compatible with glass and steel substrates. Glass is the common material used onto the solar cells surface and steel as the support structure of the PV solar panels. Besides the unique coating displaying properties such water repellence, is of utmost relevance to be self-cleaning. Self-cleaning property prevents dirt from forming an intimate contact with the surface, while the superhydrophobicity makes the water repellent. So, through this coating is possible to maintain glass and steel substrates from PV solar panels always clean. It is also intended to attain a coating which is light transmitting – anti-reflective - and which do not affect substantially the efficiency of the solar cells. Another advantages are to obtain an inexpensive coating with easy application and simple fabrication.

1.3 Motivation

This MSc thesis is extremely relevant to the PV market and to the industry within. Solar energy is an inexhaustible source, environmentally friendly and is quickly evolving concerning prices and efficiency, being a renewable energy source to invest in. This source of energy should be improved and better and innovative solutions are needed to be optimized. The deployment of protective coatings can be extremely useful not only to avoid expensive maintenance, but also to fix and create photovoltaic solar panels that operate with increased and constant efficiency due to the self-cleaning property of the

applied coatings. It is also important to mention that the unique property of the coating, which is expected to be compatible with steel and glass substrates, will be an economical choice because instead of using two coatings it will be possible to use only one for both materials and the maintenance costs decreases.

To be a part of this bright idea and also to have the opportunity to do experimental work in Centro de Química Estrutural from Instituto Superior Técnico is something which make me more motivated about this project. Besides, I was searching a theme that put together my Bachelor (Chemistry and Biological Engineering) and my Master (Energy and Management Engineering) background. However, I have noticed that most of my work will be new to me, which is also an adventure to embrace. Furthermore, to have Prof. Fátima Montemor as a supervisor is also a privilege.

1.4 Thesis outline

The Master Thesis structure is composed by: an Introduction, State of the Art, Experimental methods, Results and Discussion, Economic Methodology and Assessment, Conclusions and Futures Perspectives. An outline of each chapter is presented below:

- **1st chapter:** Introduction is subdivided in four sub-chapters where firstly is described the photovoltaic solar panels maintenance problem, afterwards through the aim of the thesis is given a unique coating as solution to this problem. Furthermore, is presented what captivate me to do this MSc thesis and the structure ensemble of the Thesis.

- **2nd chapter:** State of the Art addresses the importance of the photovoltaic solar energy and how the coatings can make a difference in the maintenance of this type of renewable energy. Initially was described the photovoltaic solar energy potential and defined what photovoltaic devices due. In order to know the developments made until today, was presented the solar cells history, the main countries and companies producers and explained how China achieved the largest capacity and production in this field. The coating is to be applied in photovoltaic solar cells, so the structure of each type of solar cell was explained. The PV power systems indicate the range of temperatures that each solar cell can sustain and the advantages and disadvantages of each system. Taking into account that is studied an environmental friendly way of producing energy, it is important to do a quick view of the sustainability and for that reason the life cycle assessment (LCA) of each type of solar cell is presented. The most important indicators are: the energy payback time (EPBT) and the greenhouse gases (GHG). The access and availability of the sun depending of his latitude around the world, the maintenance regularity recommended for each PV solar panel depending on the exposed weather conditions and the types of maintenance are fully described. Moreover, the coating maintenance, his unique functional properties (compatibility, superhydrophobicity and self-cleaning) and how to fabricate one is explained. Since I am in an Energy and Management Engineering Master was investigated the energy applications for this coating.

- **3rd chapter:** Experimental methods – The sol-gel route was used to produce the coating and for this reason each step of the process is explained. It addresses the precursors used, the dependence of the catalyst, solvent, pH, H₂O: Silane molar ratio and the hydrolysis and condensation reactions. The coating application procedure, over each substrate was done by dip-coating and spray coating techniques and the chemistry behind the curing conditions adopted is explained. A final table with all the coating trials is presented. The methodology used in the characterization techniques is described. Firstly, the contact angle measurements made through Sessile Drop Method in a Goniometer, the Optical and Scanning Electron Microscopy details, transmittance measurements through UV/Vis Spectrometer and finally the definitions of the performance parameters, how the I-V measurements were done, the experimental setup and the equations used to compute the efficiency from organic solar cells.

- **4th chapter:** Results and discussion – starts with an overview of the experimental results obtained and the best ones are selected. A comparison of the contact angle measurements with different molar ratios between TMOOS: TEOS is presented and compared considering a coating with and without modification of silica nanoparticles. The effect of pH and different molar ratios of TMES: TEOS are also discussed. Moreover, a comparison between the three best precursors – TMOOS, TMES and HMDS - was made. The TMES precursor, which presented the functional properties wanted and revealed better results in glass slides and steel substrates was studied in more detail. The contact angles achieved through Sessile Drop Method and by spray and dip-coating application route were determined on glass slides, steel and a commercialized PV solar panel. A characterization by Optical Microscopy and Scanning Electron Microscopy (SEM) was performed to compare the TMES sol-gel coating and TMES sol-gel coating modified with silica nanoparticles. The transparency of the coating was examined through percentage of transmission measurements of TMES sol-gel coating and TMES sol-gel coating modified with silica nanoparticles. Finally, a solar cell efficiency evaluation is made to organic solar cells coated and uncoated. Two solar cells are used: one which is applied TMES sol-gel coating and another with TMES sol-gel coating modified with silica nanoparticles. Through this evaluation is seen how the coating affects the performance parameters of a solar cell – V_{oc} , I_{sc} , FF and η .

- **5th chapter:** Economic Methodology and Assessment - the use of coatings instead of manual maintenance in PV solar panels – An economic assessment was done in order to know if the coating maintenance is beneficial and viable. The viability from the investor perspective and respective benefits were presented. After selecting the optimized coating, it was studied through a case study the costs of using coating maintenance. Moreover, was compared the expenses, costs savings and energy gained of using coating maintenance instead of manual maintenance.

- **6th chapter:** Conclusions – This chapter presents if were achieved the goals. The steps taken along the MSc thesis to obtain the desired novel coating. The results obtained in the contact angle measurements, percentage of transmission and efficiencies. Then, it is presented the costs of

applying the unique coating to a large-scale PV solar plant of Martifer Solar. The cost saves and energy profit gained by using coating maintenance were taken into consideration. The final conclusions from these studies is presented.

- **7th chapter:** Future perspectives and suggestions for future work directions.

2. State of the art

2.1 Photovoltaic solar energy

2.1.1 The largest energy resource

In present days, a concern that comes with increasing population is the scarcity of the fossil fuels (coal, natural gas, oil and uranium). Renewable energies sources (sun, wind, water and biomass) are an answer for the huge request of energy consumption and to attenuate environmental concerns [12, 13].

Sun is by far the most powerful and unlimited energy resource. This is due to the fact that solar energy available on earth is around 10000 times the energy consumed by the human species and that sun as energy source has been available for more 5 billion years [12]. For this reason, solar sources amongst all possible renewable energy sources, are the ones that present the greatest potential to generate energy [14]. Figure 1 demonstrates that the quantity of non-renewable energies is completely consumed, and the production of renewable energy is much higher compared to the world energy requirements. Besides these factors, figure 1 intends to show that solar radiation and respective energy generation potential are much higher compared to all the other sources of energy [13].

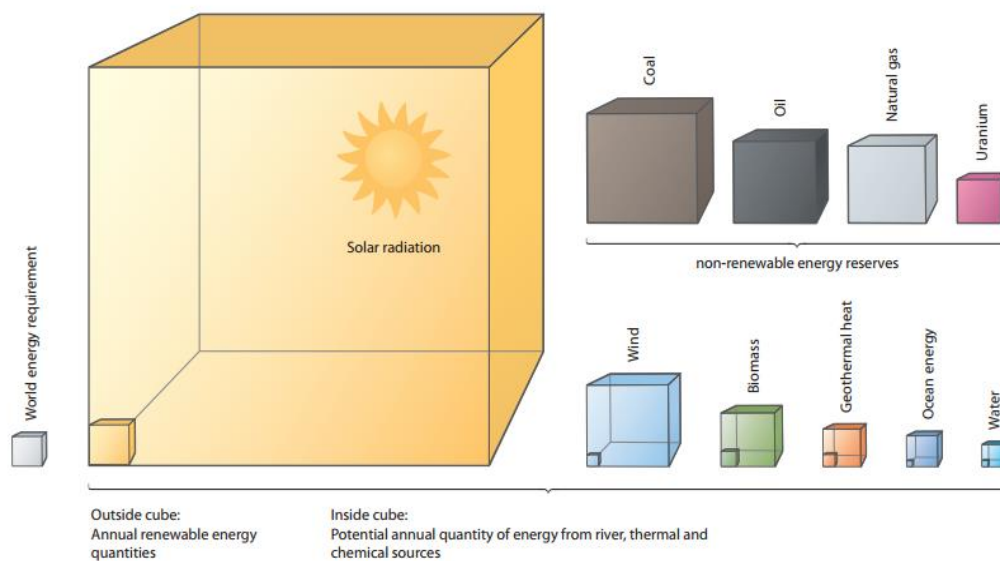


Figure 1 - Annual renewable and non-renewable energy quantities produced and potential generation comparing with world energy requirement and the solar radiation supplied [13].

Photovoltaic (PV) technology is used to produce energy from sun, a renewable source. PV will have a strong impact in the near future due to the availability of solar energy and due to the environmental friendly way to produce electricity. Concomitantly, more developments should be made to reduce the investments and maintenance costs related to PV production and to improve power conversion efficiency. However, this technology presents acceptable energy conversion losses and greater potential compared to alternative energies which don't use direct solar radiation as source. The explanation for these statements is given by the second law of thermodynamics – energy conversion gives energy losses [14].

2.1.2. Solar cells development- PV history and Market

Through the PV devices, solar radiation is converted into electric power by the photovoltaic effect. In this process, solar cells absorb photons from sunlight in a semiconductor diode and release electrons in form of electricity [15]. The PV system, in order to produce more energy is connected by series and/or parallel arrangement of cells which form the PV panel. The solar energy incident per unit area on the solar panel is designated as solar irradiance (kWh/m^2). Electrical energy is produced as output of the panels and delivered to the grid. In order to connect the panels to the AC electrical grid is necessary to use an inverter [15, 16]. The electrical power generated is measured in Watts (W) and in the absence of light the direct current (DC) generated stops. Solar cells are an energy production system and do not store energy and cannot be recharged as in common batteries [12, 17].

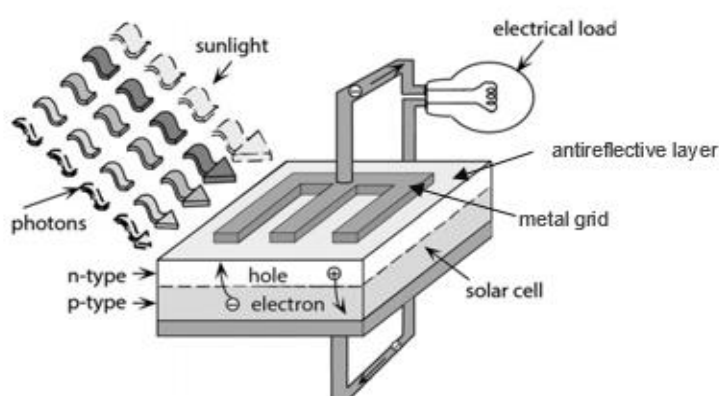


Figure 2 – Representation of a simple solar cell when operating [18].

Solar cells were created by the French physicist Alexandre Edmond Becquerel in 1839, who discovered the PV effect while was studying the effect of light on electrolytic cells. To achieve better efficiency a huge progress occurred in this field. However, only since 1950s the solar cells entered a fast development. The main reason was due to NASA (National Aeronautics and Space Administration) application of crystalline silica (c-Si) solar cells with an efficiency of 6-10% into satellites and space programs. An improved solar cell was created by Bell Telephone Laboratories in 1954. This modern solar cell was grouped in a solar module, with complementary components such as controllers, inverters and so on [19, 20].

In the 1960s solar cells research was focussed on compound semiconductors (III-IV and II-VI). In the same decade, there was an improvement on the know-how on polycrystalline Si (pc-Si) and thin-film solar cell technologies which allowed to new advances, such as: increase of the production capacity, decreased material consumption and development of fabrication processes with a lower energy input. Through deposition processes it was possible to integrate solar cells into a structure of modules which allowed the large-scale terrestrial widespread with cost reduction, and the opportunity to achieve a better cost-effective photovoltaic solar energy production [20]. Furthermore, technology, research and development (R&D) showed important evolutions and large volumes of silicon cells started to be manufactured in 1970s and early 80s. The industry started to mature and focussed into growing manufacturing and costs reduction after the energy crisis in the 1970s. Nevertheless, the growth had a

relevant impact during this period of time due to the implementation of PV plants with power generation in the range of multi-megawatts. Also during the 1980s, U.S.A (United States of America) had lost their lead in the PV sector to Japan, Europe and China. The reason for this was mainly due to government investment suspension and also absence of private investment. US semiconductor companies, with decreased funds could no longer proceed with research and development or with efforts to work on this area. Consequently, the companies and their technologies were bought by foreign companies from Japan, Europe and later to China [12, 20, 21].

Afterwards, during 1990s, organic and dye-sensitized solar cells (DSSCs) technologies emerged. The DSSC stood out as an important nanoscience and innovation within the photovoltaic technology. Some of the advantages from DSSCs are the high efficiency of up to 11%, low-cost potential that is lower than 0.7 euros per peak Watt (€/Wp) and a lower payback time, of less than half a year [19, 20]. Currently, the PV market growth rate is similar to that of the computers and telecommunication sectors. There is an exponential market production of photovoltaics, which in 2009 achieves high annual rates of about 30 to 40% and the world PV production increased to 10.66 GW. Nearly half of the PV market is centralized in rural applications and the second main market is the industry (consumer applications, grid-connected systems, developing countries and remote industrial systems). PV applications are being developed year by year mainly in USA, Japan, European Union (mostly in Germany and Spain) and China/Taiwan [19, 20].

Almost 50% of the world production of PV cells and modules in 2009 is presented on Table 1 [19].

Table 1 - Main countries producers in 2009 and the respective annual production of PV cells and modules (MW)
(Adapted from [19]).

Main Countries Producers	China/Taiwan	European Union Countries	Japan	United States
Annual production of PV cells and modules(MW)	5190	1930	1500	595

The largest producing companies in 2009 are shown on Table 2 and is possible to conclude that SunTech Power from China was the world biggest producer [19].

Table 2 - Main companies producers in 2009 (Adapted from [19]).

Main Companies Producers	SunTech Power	Sharp	Hanwha Q-cells	Yingly Green Energy	JA Solar	Kyosera	Trina Solar	Sunpower	Gintech	First Solar
Power Generated (MW)	704	595	537	525	509	400	399	398	368	1.011
Country where was founded	China	Japan	South Korea	China	China	Japan	China	USA	China	USA
Year of foundation	2001	1912	1999	1998	2005	1959	1997	1985	2005	1990

China, which is pursuing a policy for the Technology Innovation System (TIS) (Table 3) presently has the largest capacity and production worldwide [9]. Two of the biggest concerns from China are the

overcapacity and pressure to decrease CO₂ emissions. A way to overpass the excess of pollution is to develop a distributed PV solution for industry and domestic market and also to build PV power plants in many areas. Since 2009 until 2014, the distributed grid-connected (to the existing power grid) capacity from photovoltaics has been renovated in a sustainable structure over the years. In 2014, the distribution of photovoltaics (PV) in China had a total installed capacity of 5.15 GW [21, 22].

Table 3 - Technology Innovation System (TIS) components for China. Each component promotes the PV technology development, adapted from (Adapted from [21]).

TIS(Technology Innovation System) for China	
External Force	<ul style="list-style-type: none"> ☞ Abundant solar resources (Average annual solar radiation that reaches the earth surface=50,9 MJ); ☞ Global PV market increasing: price drops and efficiency of PV increases; ☞ Oil price increases and climate changes promote the fast development of PV technology;
Government	☞ Financial support to the R&D of PV and subsidized capital cost of the equipment in Western China remote rural areas;
R&D	<ul style="list-style-type: none"> ☞ Highest efficiency in single c-Si and pc-Si solar cells; ☞ Huge progress in thin-film solar cells;
Manufacture	☞ Biggest world PV cells manufacture in 2016 – Trina Solar;
Market	☞ Focused on communications, remote areas, rural electrification and 80% of Chinese cells are exported (mostly to Europe and USA);

According to Information Handling Services (IHS), the global solar PV production is increasing all over the years and in 2015 achieved 140 million TWh and is forecasted to reach around 148 million TWh this year [23]. In 2016, China still has the largest global market of PV production. The most recent updated data from HIS indicates that 50% of the global market share is composed by six Chinese companies. These companies are named the “Silicon module Super League” and the ranking from the first to the six place is: Trina Solar, Canadian Solar, Jinko Solar, JA solar, Hanwha Solar (combines Hanwha SolarOne and Hanwha Q-cells) and Yingli Green Energy. Currently, belongs also to the top 10 the Sharp, Renesola, First Solar and Kyosera companies. In 2009, five companies from the top 10 ranking were from China and today seven belong to the top 10. Besides, three Chinese companies belong to the top 6 in 2009 and in 2016 all the top 6 companies are Chinese. During this time interval TIS implemented was essential. So, China since 2009 is an ascending market in this field and the forecast from IHS reports show that the installed capacity is still increasing in the next years [23]. In respect to the types of solar cells technologies used these days in the PV industry, is mainly focused in c-Si and pc-Si wafers technologies. Cadmium telluride (CdTe) cells are growing in the market and the solar cells that are slowly integrating the market are the thin-film CIGS (cooper-indium-gallium-selenide) and amorphous silicon solar cells (a-Si based). Thin-film PV technologies are expected to dominate the solar cells market in the next years [18].

2.1.3. Types of solar cells

This subchapter overviews the different types of solar cells with relevance for implementation of PV solutions over the years [18]. Both variety and quality of the solar cells has increased significantly.

The selection of solar cell materials is mostly dependent on fabrication cost and on the absorption characteristics match with the solar spectrum. Solar cells technology can be divided into three generations – table 4 [18, 24]:

- 1st Generation - constitutes the type of solar cells which dominates the industry and includes: wafers of single and polycrystalline silicon that account for 90 and 55% of the market share respectively, in 2014. Silicon presents many advantages such as being abundant, non-toxic and has advanced knowhow, but is too expensive for large scale production;
- 2nd Generation - composed by thin-film amorphous, polycrystalline and monocrystalline semiconductors. These cells use cheap substrates or superstrates (e.g. a-Si, CdTe (cadmium-telluride) and CIGS (copper indium gallium di-selenide) cells);
- 3rd Generation - accounts for the multi-junction technology (solar cells that are in R&D phase), such as dye-sensitized(DSSC) and organic solar cells, besides the concentrated photovoltaic (CPV) which is already in the market;

Table 4 - Types of solar cells and respective efficiency, market share, PV module size and output power (Adapted from [24]).

Type of solar cell		Average commercial efficiency w/ air mass 1.5 (%)	Maximum PV module efficiency (%)	Market share in 2014(%)	PV module size(m ²)	Maximum PV output power (W)
1 st G	Single crystalline silicon(c-Si)	17	25	90	2	320
	Polycrystalline silicon(pc-Si)	14	20.4	55	8	_____
2 nd G	Amorphous Silicon(a-Si)	6.5	12.2	32	1.4	300
	Copper Indium Gallium Di-selenide(CIS/CIGS)	9	19.8	25	0.6-1.0	120
	Cadmium Telluride Cells(CdTe)	9.5	19.6	43	0.72	120
3 rd G	Concentrated Photovoltaic (CPV)	27.5	40	_____	_____	120
	Dye-sensitized (DSSC)	3	_____	_____	_____	_____
	Organic or Polymer(OPV)	1	_____	_____	_____	_____

The 1st and 2nd Generation of solar cells are commercially mature and are produced in large scale. These solar cells are composed of c-Si or a-Si which has the highest and the lowest efficiency, respectively. Efficiency is highly dependent on temperature and the commonly chosen operating

temperature for solar cells is about $45^{\circ}\text{C} \pm 2^{\circ}\text{C}$. However, the operating temperature also depends on manufacturer specifications. The selected operating temperature is according to the nominal operating cell temperature (NOCT) which is when the irradiance is 800 W/m^2 , wind speed is 1 m/s and the ambient temperature is 20°C . The cell temperature not only affects the efficiency, but all performance parameters, such as: maximum power (P_{max}), open circuit voltage (V_{oc}), short-circuit current (I_{sc}) and fill factor (FF). It was experimentally tested that with increasing temperature the performance parameters decrease [25, 26]. Besides, the high solar radiation and high temperatures at the panel surface are responsible for degradation mechanisms which decrease the efficiency [25, 26].

Dust is also a strong contributor for lowering the PV output, by attenuating irradiance in a spectrally dependent manner. Each PV technology has different responses to adversities such as dust because the spectral transmittance affects various spectral response shapes differently. The type of solar cells with wider band-gap such as a-Si and CdTe technologies display worst response for a dust concentration of 4.25 mg/cm^2 compared to c-Si and CIGS technologies. The photocurrent reduces 33% for a-Si and CdTe technologies and 28.5% for c-Si and CIGS solar cells [25, 26, 27].

Besides yield, the costs of the equipment and maintenance are important to taking into account. Presently, the 1st Generation represents the cheapest PV module cost with 0.64 €/W and the 2nd Generation with 0.73 €/W for a-Si, 0.83 €/W for CIS/CIGS and CdTe solar cells. Another aspect that is important to mention is that the cost of fabrication and the yield obtained from each solar cell depends on the substrates and superstrates and overall constitution of each solar cell (figure 3) [24].

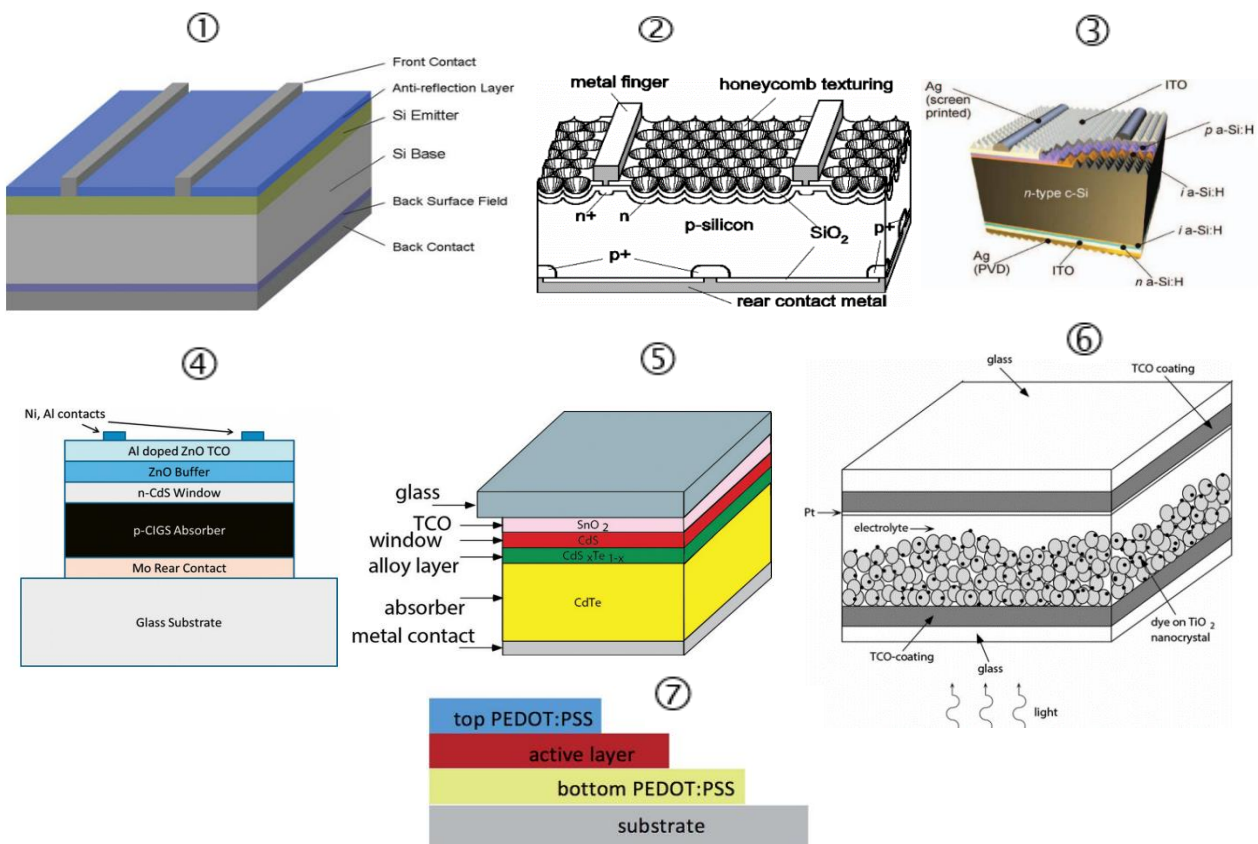


Figure 3 - Schematics from solar cells structure: 1- single crystalline silicon solar cell [28]; 2- polycrystalline silicon solar cell[29]; 3- Amorphous silicon solar cell [30]; 4 - copper indium gallium di-selenide (CIGS) solar cell [18]; 5- cadmium telluride solar(CdTe) solar cell [18]; 6 - dye-sensitized(DSSC) solar cell [18]; 7-organic solar cell [31];

It was also important to mention that a group of solar cells forms a module and several modules assembled into a single structure is a PV solar panel. In a PV solar plant there are many panels disposed in an array (assembly of panels connected in series) that constitute the generator or photovoltaic field when the assembly of arrays is connected in parallel to obtain the required power output (figure 4) [32].

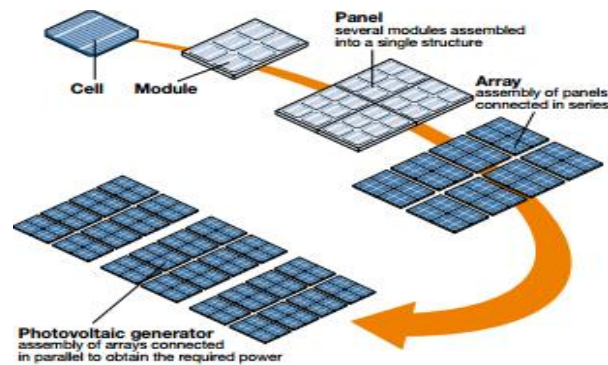


Figure 4 - Schematic of the PV solar panels disposal [32].

2.1.4. Photovoltaic systems – PV and CPV

After a brief explanation from each type of solar cells, it is important to define the types of solar power systems where they can be installed in. The application of this MSc thesis it is in photovoltaic solar cells so it is also important to focus on the PV systems which the PV solar cells are involved in. Firstly, a PV technology works with a direct solar power system which converts directly solar energy into electricity by using a solar cell. PV systems can be divided in concentrating photovoltaic systems (CPV) and in non-concentrated PV systems. CPV systems operate by using an optical assembly (lens and curved mirrors) to concentrate light onto a multi-junction PV cells which are highly efficient and non-concentrated PV system operates by using a PV cell but without the optical assembly. Besides the large areas of the CPV systems technologies allowing to have higher energy absorptions into a small cell it also operates in an irradiation level many times greater than that of non-concentrated PV systems, so the PV cell's conversion efficiency is greater in the first case [33].

Another beneficial aspect about the CPV systems is the little output degradation with increasing ambient temperatures and are economically viable for hot and dry desert conditions where daytime temperatures can surpass 50°C. The CPV systems can still work with temperatures above 80°C and usually non-concentrated PV systems can only work until 80°C [16].

However, the CPV systems have higher capital cost and the PV systems are more developed and have better know-how compared with CPV systems. These characteristics allowed to have more inexpensive and sufficiently efficient choices for PV systems [33].

CPV systems can be applied in any of the concentrated power systems (CSP) types, such as: linear Fresnel reflector (LFR), parabolic trough, central receiver (solar tower) and parabolic dish – figure 5 [24]. The concentrators are, however, designed specifically for the CPV application. CSP is an indirect

solar power system which firstly converts solar energy to heat by the efficient use from the thermodynamic cycle and afterwards generates electric power and CPV systems convert directly solar energy into electricity through photovoltaic effect [33].

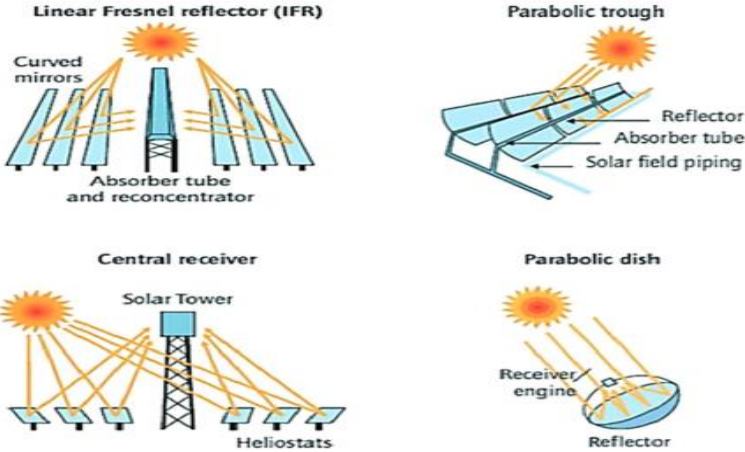


Figure 5 - Main CPV technologies [24]. Adapted from International Energy Agency (IEA).

Another important concern when assessing the life cycle and the energy payback time from a CPV system is the accumulation of dust on the lens. There are losses of many light beams which do not reach the cell due to the scattering effect on the lens. The losses in concentration modules due to dust is worse comparing with flat modules [24].

Selection between PV and CPV systems depends from each specific case and given conditions [24, 33]. Table 5 depicts the overall advantages and disadvantages from each system [24].

Table 5 - Overall advantages and disadvantages on PV solar systems (Adapted from [24]).

Photovoltaic solar systems		
PV system	Advantages	Suitable for areas having low as well as high direct irradiance; A larger number of PV systems can be installed in a small land comparing with CSP and due to this have better performance (better capability and electricity production); Suitable for large and small applications;
	Disadvantages	Higher environmental impact due to the hazardous materials used for cleaning;
CPV system	Advantages	Higher efficiencies; Higher annual electricity production; suitable for areas of high direct irradiance.
	Disadvantages	Only uses direct component from incoming solar radiation(loss from diffused and reflected components); Higher capital cost(not suitable to small scale solar power plants);

2.1.5. Overview into PV solar energy sustainability

Photovoltaic solar energy is commonly claimed as one of the cleanest technologies for power generation. However, manufacturing PV modules is the major contributor to the total lifecycle impacts of a solar PV system. The main advantages are solar electricity's lower GHG intensity and lifecycle energy use compared to traditional fossil-based power plants [34]. Sustainability and environmental performance can be measured for five types of solar cells (mono-Si, multi-Si, a-Si, CdTe and CIS) through the life cycle assessment (LCA). The LCA is usually conducted to evaluate the environmental impacts during life cycle. The environmental indicators used to evaluate the performance from PV systems are: energy payback time (EPBT) - years required to generate a certain amount of energy (measured with equivalent primary energy) which compensates the energy consumption over its life cycle - and greenhouse gases (GHG) emission rate (g CO₂-eq./kW h). EPBT and GHG emissions variation depends of several factors, such as: the solar cell type, module type, manufacturing processes and technologies, installation methods and locations, location weather conditions, estimation methods, etc. [34, 35].

Amongst the 1st and 2nd generation of solar cells, the CdTe thin film PV technologies give the best environmental benefits and the mono-Si the worst. Despite the mono-Si presents a highest efficiency in compared to other solar cells, it has also the highest life cycle requirement. Thin film PV systems, especially CdTe and a-Si solar cells have the lowest energy demand. The EPBT from CdTe PV system is also the shortest due to the lower energy demand and relatively high conversion efficiency. In case of a-Si, the EPBT is high due to the low conversion efficiency. For the GHG emission rate mono-Si generates more GHG emissions during its life cycle because of the high energy intensity of solar cells production processes. In general, CdTe possesses the shortest EPBT and the lowest environmental impacts (lowest GHG emissions), with 0.75 years and 10.5 g CO₂- eq./kW h, respectively [36]. Previous studies demonstrated that PV technologies are sustainable and environmental-friendly regarding the measured EPBT and GHG emission rate. The environmental indicators of each solar cell type are presented on Table 6 [34]. Take into account that the lifetime of a PV solar panel is between 25 to 30 years, through the LCA is possible to confirm that all the solar cells are sustainable [34, 35].

Table 6 - Reported values of EPBT, GHG emission rates and primary energy requirements of different types of solar cells (Adapted from [34]).

Environmental Indicators and life cycle energy requirement	Types of solar cells		
	Mono-Si	Multi-Si	Thin film(a-Si, CdTe and CIS)
EPBT(energy payback time)- years	1.7 – 2.7	1.5 – 2.6	0.75- 3.5
GHG emission rate – g CO ₂ -eq./kW h	29 -45	23 - 44	10.5 - 50
Primary energy requirement – MJ/m ²	2860-5253	2699-5150	710-1990

2.2 Maintenance of solar panels

2.2.1 Access and availability

Sunlight is not equally distributed on earth's surface, as it is observed in Figure 5. Nevertheless, one hour of energy received from the sun is equivalent to the energy requirements of approximately one year [12].

The solar energy resource is dependent on the latitude (figure 6) [12]. For this reason, the European South countries (Portugal, Spain and Italy) present the highest annual solar irradiance and the North of Europe countries (Norway, Sweden and Denmark) the lowest annual solar irradiance availability. Germany, is the European country with the largest power installations from photovoltaic systems, however is not the country with highest amount of annual solar irradiance in Europe. Portugal is the European country with the best photovoltaic solar electricity potential because it is one of the countries with highest annual solar irradiance in Europe [17].

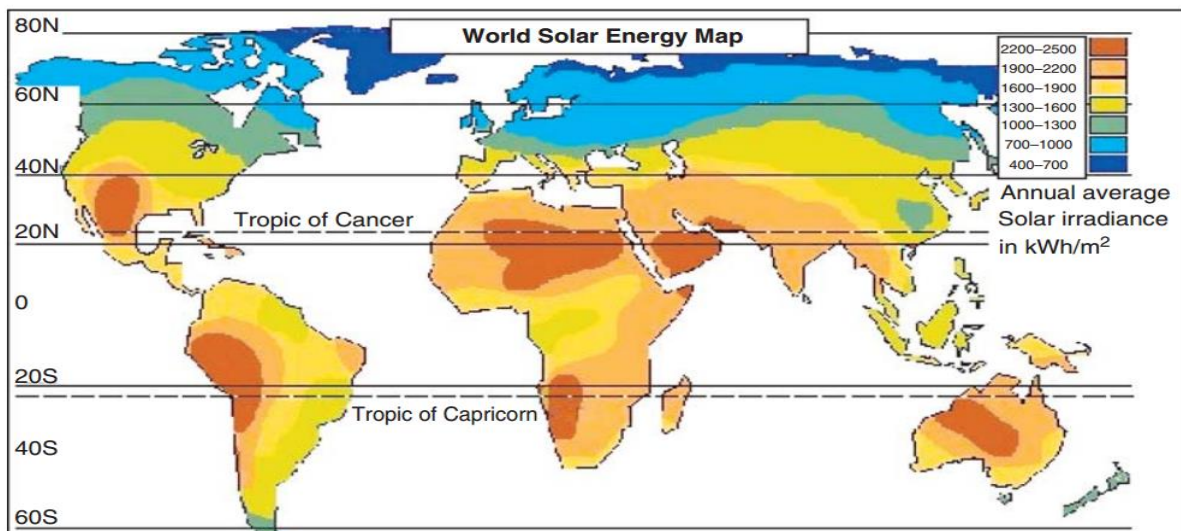


Figure 6 - Annual average solar irradiance (kWh/m²) distribution around the world [12].

Between 35°N until 35°S (low latitudes) arid and semi-arid areas receive the highest direct normal irradiance (DNI) - amount of solar irradiation received per unit area by a surface that is always held perpendicular (or normal) to the rays that come in a straight line from the direction of the sun at its current position in the sky. Large-scale solar plants are usually located within these latitudes, including in seven of the world's deserts. Deserts and arid zones, besides the benefit of high availability for solar energy conversion due to the large amount of sunlight have also environmental drawbacks. The disadvantages are: high ambient temperature (risk of destroying the array due to excess of output current) and high concentration of atmospheric dust (minute solid particles with diameters less than 500 μm in diameter) [1].

China, Europe, Middle East, Australia and U.S.A have already installed large-scale solar installations and most of them are located in deserts. Desertec mission intends to provide electrical energy through solar radiation from North African and Middle Eastern (MENA) countries to supply the largest power requirements on earth and 15% of the electricity requirements from Europe by 2050. In order to produce the higher amount of electrical energy in less time is important to focus on the obstacles, such as the transmission losses from PV and CPV systems and reflection losses from CSP systems [1].

Dust deposition in solar panels optical surface is one of the main causes contributing to decreased efficiency which can be actually controlled. It is not possible to control weather conditions, is not either possible to control some of the efficiency losses due to thermodynamic causes or even other natural adversities. However, it is possible to improve routes to maintain solar panels clean and in better cost-effective procedures [1, 36, 37].

Dust, bird-dropping, soot, growth of organic species, contamination by plant products and water-stains (salts) deposition on the PV panels decreases the energy yield and consequently affects the overall performance of the PV system. Particulate contamination into optical surfaces is denominated as the “soiling” effect and brings the disadvantages mentioned before due to scattering and absorption losses of the incident light, which consequently gives output power losses. PV installations have module efficiencies usually around 10 to 25% due to losses in the wiring, inverter and due to the big impact of “soiling” effect. In order to avoid the accumulation of dust deposition is important to manage the maintenance of solar panels. However, some of the large-scale solar plants are located in places with hard water access. It is important to remind that water is in the opposite situation from the solar energy resource, because is a limited resource and in many countries water scarcity hardly justify its use as “cleaning material”. In order to clean the solar panels, water should be free of salt detriments. Besides this, in some places the rain is scare and hardly predictable and is probable to rain only a few times per year, making maintenance more difficult. Transport of water into remote or deserted areas is very expensive and will not be possible to have a payback from the solar plants with this alternative. If water is a limited resource it turns to be the most expensive part of the solar panels maintenance, after the cost of labour. For this reason, is important to find cleaning alternatives and water independent. Another factor to have into account is that dust settlement depends on two main factors, which are: the location from the solar plants and the climate behaviour [1, 2, 36, 37, 38, 39].

2.2.2 Cleaning Frequency

How many times we should clean a solar panel? The answer is not the same to all the cases. Each case has a specific way to manage the maintenance. Firstly, is unavoidable to think about the cost of labour, cost and access to water resources, cost of materials and equipment and the loss of energy efficiency. Cleaning frequency is dependent on: atmospheric dust concentration, the site characteristics (e.g. vegetation nearby, pedestrian and vehicular traffic, volcanic eruptions and air pollution), weather conditions (e.g. ambient temperature, humidity and wind pattern). More specifically, high-speed wind regime helps in the removal of dust, PV system tilt-angle (horizontal surfaces

accumulate more dust than inclined ones, due to gravity effect), less sticky and smoother surface of solar panels accumulate less dust. Accumulation of dust should be avoided because dust promotes dust and finer particles have more deteriorating effects due to a more specific surface area which causes more scattering losses [1, 37].

A cleaning cycle is stipulated for each PV system. In order to answer this question, PV installations can be divided into three regions: low-, mid- and high-latitude regions. As discussed before, a lower tilt-angle will tend to accumulate higher dust deposition and it requires more cleaning cycles. PV solar panels located in regions with low latitudes require low tilt-angles to achieve maximum solar gain, in mid-latitudes they are required to have higher tilt-angles and in high latitudes the tilt-angles are nearly vertical. For example, between 15° to 25° in northern and southern hemispheres there are dry tropical zones characterised by frequent dust events and lack of rainfall. Dust events require at least weekly cleaning but in case of dust storms in deserts with high levels of air humidity (formation of mud into solar panels surface) should have an immediate cleaning (application of dust-repelling coatings is an alternative to avoid the constant need for cleaning). A weekly cleaning is recommended when there is lack of rainfall. In regions where there is regular precipitation expected, natural cleaning by rain restores PV cell efficiency (e.g. wet tropical climates). Regions with higher dust accumulation, due to proximity to industries, require a daily cleaning. In case of regions prone to higher dust due to human activities require weekly cleaning. In high latitudes there are regions where snowing is frequent and snow should be immediately cleaned from solar panels surface [1, 37, 39].

2.2.3. Types of cleaning processes

Cleaning processes can be divided into: natural, manual, automatic and passive methods. Natural cleaning processes are dependent on rainfall, wind, gravitational forces and other natural events. Nevertheless, rainfall is the most efficient natural cleaning agent to remove dust from solar panels surfaces. Some countries are provided with periodic washing of the surfaces via helpful weather patterns (e.g. Leuven, in Belgium and Bern, in Switzerland) and is unnecessary regular manual surface cleaning. However, in other regions, the weather assistance is not widespread and is necessary human intervention to help cleaning the surfaces [1, 39].

Wind is other natural event that can promote the removal of dust from PV surfaces but can also bring dust, so it has a dual effect. Besides, in the case of crystalline silica(c-Si) solar cells, when wind velocity increases, the cell temperature decreases and that improves the efficiency of the system. Another benefit is that higher wind velocity reduces the ambient relative humidity being possible to achieve higher cell efficiencies [1, 39]

Adhesion of dust to the surface of PV solar panels can also decrease efficiency due to higher wind velocities that dries the moisture layer formed between the dust particles and the surface. PV solar panels can be installed at a higher level above ground (wind speed increases with height) to take benefit of the wind speed. Nevertheless, wind cleaning effect cannot remove particles smaller than 50 µm and in a dusty environment wind will deposit more dust on a PV module. In some regions where

there is no weather assistance, this natural cleaning process cannot be applied and manual cleaning process is an option [1, 39].

Manual cleaning maintenance normally makes use of a solution of demineralized water and detergents to clean efficiently the PV surfaces and then the surface is wiped with soft cloth. This manual maintenance process is mostly used in small-scale installations. In large-scale PV plants the adopted procedure includes high-pressure water jets with anionic detergents and brushing afterwards. In all type of installations, it is recommended to clean early in the morning when the mirrors are wet, because dust is easy to remove from the coatings or uncoated surfaces without damage. Of course, the manual cleaning process has the disadvantage that repeated wiping or brushing can cause scratches and damage the surface. Labour and water resources are the most expensive part of cleaning and automated cleaning systems contribute to decrease this expense by using computer-controlled mechanical devices [1, 19].

Automated cleaning systems use a single axis sun tracking system equipped with a cleaning mechanism. In this case, cleaning and scrubbing can be automated and can rotate until the PV surface being turn down to avoid dust depositions due to storm weathers and the PV solar panel can rotate 360° to be possible to change the angle in anyway necessary, such as being perpendicular to the ground to remove the dust. The rotation from PV solar panels complement the “job” made from PVCleaner Robot (PV surface cleaning robot) – composed by one cleaning head moving and brushing upward and downward and also moving trolleys placed on top and bottom part of the panels. However, this procedure also needs maintenance and water (systems without use of water are still in development) as a resource to clean. The solution may reside on desalinated water (expensive and is not available in all the locations) or water tanks (risk of water evaporation with high ambient temperatures). The automated cleaning processes need trained people to maintain the cleaning robots and the costs are enormous, especially in remote areas. Other cleaning processes, named as passive methods are: electrodynamic screens (EDS) or anti-soiling coatings (also called as self-cleaning coatings) [1, 40].

Electrodynamic screens (EDS) uses the electrostatic force to repel particles and the sand that are transported to the cover glass of the solar panel. This cleaning method doesn't need water resources or labour for operation and maintenance. It is a cleaning system suitable for mega solar power plants constructed in deserts, because is a potentially inexpensive technique. Although, this is a method that is still in the developing stages and is not fully established yet [1, 40].

Ultimately, anti-soiling coatings are a passive surface treatment used to remove dust from solar power surfaces. Anti-soiling or self-cleaning coatings can also decrease the transmission losses from solar panels. If a textured glass is used as front surface for PV modules the reflection losses will decrease and the performance will increase.

Coatings improve the cleaning efficiency of natural cleaning agents, have a lifetime of some years and can bring some beneficial properties depending on the application. The coating must be durable, should resist to high temperatures, sandstorms and ultraviolet radiation. Other characteristics which are desirable are: low price and facility to be applied on different types of solar systems [1, 40]. Table 7 synthetizes the advantages and disadvantages from each cleaning process [1] .

Afterwards, it will be explained in more detail the use of self-cleaning coatings and the unique coating solutions developed in this master thesis.

Table 7 - Advantages and disadvantages of different cleaning methods for dust removal from PV module surfaces (Adapted from [1]).

Cleaning method	Advantages & Disadvantages
Natural Cleaning	<u>Advantages:</u> No cleaning costs; efficiency of the solar panel can be restored through heavy rain and melting snow; removal of large dust particles from PV solar panel surfaces through high wind.
	<u>Disadvantages:</u> Dust deposition and efficiency is reduced by light rainfall in dusty atmosphere followed by dusty wind.
Manual cleaning by high-pressure jet	<u>Advantages:</u> cleaning can be performed whenever required.
	<u>Disadvantages:</u> Expensive cost of labour and water resources; requires trained personnel; water resources are very limited in arid zones; surfactant used for organic film removal are harmful to the environment.
Automated cleaning by controlled water spray	<u>Advantages:</u> when the water cleaning process is used reduces cell operating temperature and increases efficiency; can be activated by using a pump automatically or manually.
	<u>Disadvantages:</u> not convenient for large-scale PV systems; scalability of the method is not cost-effective; water resources and surfactant are needed; does not provide uniform cleaning over the entire surface; loss of water by evaporation.
Robotic cleaning system	<u>Advantages:</u> both cleaning and scrubbing processes can be automated; efficient water usage systems have been utilized for economical cleaning.
	<u>Disadvantages:</u> needs water resources/surfactant for cleaning; it needs a team of technicians for supervision of robot operation; not cost-effective in some applications due to the power consumption of the robotic device; high operation and maintenance costs.
Anti-soiling coating	<u>Advantages:</u> improves cleaning efficiency of natural cleaning agents; lasts for some years; effective method for making the surface either highly hydrophobic or hydrophilic; avoids dust deposition and enhances efficiency from PV solar cells.
	<u>Disadvantages:</u> dust adhesion is greatly dependent upon the electrostatic characteristics of the film and dust; greatly site-specific.
Electrodynamic screen	<u>Advantages:</u> does not need water resources or labour for operation; power consumption is very low.
	<u>Disadvantages:</u> in development stages, the durability is unknown; performance limited to relative humidity (RH) below 50%.

2.3 Unique coating with self-cleaning properties

Coatings were created long time ago to protect materials. Materials are often susceptible to prejudicial adversities from the surrounded atmosphere and may corrode. These effects result in shorter lifetime and decreased efficiency and performance of the material. Coatings play a crucial role in protecting the metal surface from the aggressiveness of the environment. Moreover, they can also provide additional functionalities to the surface of the protected materials. Coatings consists in a liquid or solid material that is applied over a substrate (e.g. carbon steel, stainless steel, glass, aluminium, stones, iron, etc.) in a continuous or discontinuous film through several application methods. These coatings can change the substrate properties, such as: corrosion resistance, reflectance, adhesion, wettability, strength, durability and more [41, 42].

Nowadays, it is difficult to find surfaces which does not have a coating applied on it. Some of the coatings applications are: in house paints, furniture, walls and ceiling paints, windows, cements, automobiles, aircrafts, paper, clothes, beverage cans, ships, mobile phones, textiles, satellites, solar panels, etc. [41, 42].

Recently, with the exponential growing market of PV solar panels, concerns related to maintenance and cleaning have increased. As mentioned in the subchapter 2.2. Maintenance of solar panels, the maintenance of solar panels is expensive and there is the need to develop cheaper cleaning processes. The application of coatings on photovoltaic solar cells can be a cost-effective and alternative solution [41, 42].

Unique, is the word which better defines the solutions presented in this work. The coating created in this master thesis is intended to be applied in photovoltaic solar cells. This coating is intended to provide superhydrophobic properties and other beneficial properties, such as being self-cleaning and anti-reflective. The final coating is expected to be compatible both on steel and glass substrates. The bibliographic revision revealed that superhydrophobic coatings already exist for different substrates. Although, most of them have not been applied in solar cells. Glass is the substrate which is more often used in different researches and some of the coatings can be applied in more than one substrate.

Literature papers showed that is scarce when one specific coating is applied on different substrates. In many cases the coating is applied on a specific substrate and the authors just mention that the coatings may be applied on solar panels, still displaying the same properties. Although, the preparation of coatings for industrial applications still requires further efforts.

There is no information on scientific literature mentioning that the same coating can be applied on different substrates that belong to the structure of a solar cell. As shown in figure 3, different types of solar cells are composed of several layers of material assembled on the top of another (superstrates). The bare substrates are usually made of glass and PV solar panels supporting structure is frequently made of steel or galvanised steel. There are only a few coatings created and applied on solar cells, but were made for a specific substrate which is glass. For other applications was also made functional coatings with the same properties. However, a coating compatible both with glass and steel and applied on PV solar panels was not done previously. The capacity to apply the same coating to both

steel and glass substrates and to maintain the beneficial characteristics mentioned above, will contribute to a unique coating solution for a non- expensive maintenance route for solar panels.

Through this new solution it will be possible to buy one instead of two coatings to use in the PV solar installations maintenance. This reduces the costs from the installation and maintenance companies.

The search results from superhydrophobic coatings with self-cleaning properties obtained on Google Scholar and Web of Knowledge shown that since 1993, and every five years, afterwards the magnitude rises. These indicates that the coatings are gaining wide attention and great progress is ongoing [43].

2.3.1. Superhydrophobic coating with self-cleaning properties

Self-cleaning coatings are labour-saving in many fields and one coating can have multiple functions. These coatings are divided into superhydrophobic and superhydrophilic categories. In case of superhydrophobic coatings, the water droplets slide and roll over the surfaces and drag away the dirt, while in superhydrophilic coatings water spreads over the surfaces thereby cleaning out dirt (see figure 7) [46]. Superhydrophilic coatings have an additional property when combined with metal oxides which is to chemically breaking down the dirt by a photocatalytic effect - sun-light assisted cleaning mechanism which can happen with dioxide titanium (TiO_2) reacting under the ultraviolet light and splitting the organic dirt. Although, in surfaces with superhydrophilicity, the rain water will diffuse to the whole surface instead of get together and it will rinse the dust. This means that superhydrophilic surfaces cannot be used in solar cell arrays because most of these surfaces are expected to work in desert regions with seldom rain [5, 44, 45].

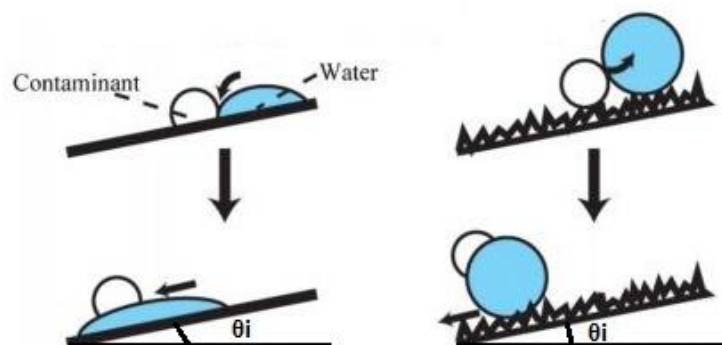


Figure 7 - Schematic representation of the self-cleaning mechanisms when the surfaces are tilted to a certain degree, denoted as inclination angle (θ_i). On the left is presented a superhydrophilic surface where the water goes beneath the contaminant and on the right is presented a superhydrophobic surface where water picks up the contaminant (Adapted from [46]).

This type of surfaces are related to the surface contact angle (θ) which is the angle formed at the three phase boundary (solid/liquid/vapour) between the surface of the solid and the surface of the liquid drop (see figure 8). Contact angle represents the degree of partial wettability of a solid surface and

represents the angle from the interface between the liquid and gas (air+ vapour) phases meets the solid surface [41, 47].

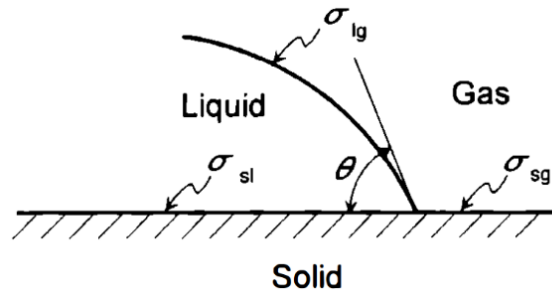


Figure 8 - Three phases in mutual contact defined by various interfacial tensions ruled by Young's equation [47].

As shown in the previous picture, the system is composed of interfacial tensions. When is established an equilibrium contact angle for a liquid drop on an ideally smooth, homogeneous, flat, and no deformable surface, as in the case of figure 8, the Young's equation can be applied – equation (1),

$$\sigma_{lg} \cos \theta = \sigma_{sg} - \sigma_{sl} \quad (1)$$

where σ_{lg} corresponds to the liquid-gas interfacial tension, σ_{sg} to the solid-gas interfacial tension, σ_{sl} to the solid-liquid interfacial tension and θ is the water contact angle. This equation relates the contact angle of a drop on a surface to the specific energies of each interfacial tension [47].

The surface wetting behavior is based on the water contact angle (WCA) and can be divided in 4 regimes: $\theta < 10^\circ$ (superhydrophilic coating); $10^\circ < \theta < 90^\circ$ (hydrophilic coating); $90^\circ < \theta < 150^\circ$ (hydrophobic coating) and $\theta > 150^\circ$ (superhydrophobic coating) – Figure 9. A superhydrophobic regime describes a state of nearly perfect non-wetting. The conditions to obtain a superhydrophobic coating with self-cleaning properties are: a WCA $> 150^\circ$, a water contact angle hysteresis (CAH) lower than 10° and a sliding angle also lower than 10° [7, 48, 49]. In case of having a superhydrophobic surface the water droplets will slide and roll-off the surface thereby cleaning them and with a minimum inclination when is self-cleaning. Through this coating application the accumulated dust of different sizes and shapes on the solar panels devices will be removed [8].

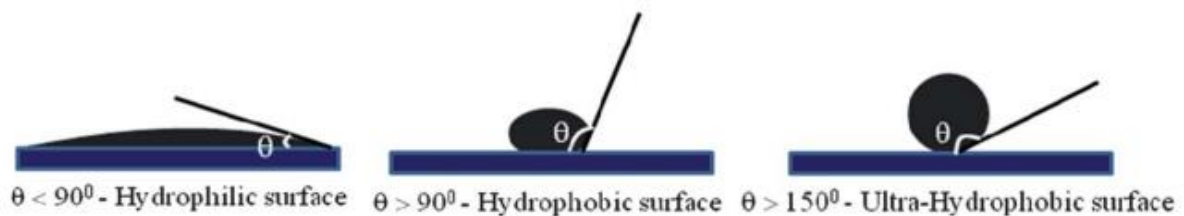


Figure 9 - Schematic with the representation of a hydrophilic, hydrophobic and ultra-hydrophobic surfaces (Adapted from [5]).

This surface is composed by a low surface energy material which has a rough surface with hierarchical micro- and nanostructures. Another important factor is the hysteresis angle that should be approximately equal to the tilting angle in order to facilitate the water droplet mobility. Over the last decade, superhydrophobic coatings with self-cleaning properties have been explored. This type of coatings has attracted huge attention on science, research and industrial areas and is precisely this type of surfaces that are intended to be produced in this MSc thesis [50, 51].

The dynamic behaviour of droplets on superhydrophobic surfaces was studied by David Quere and the highlights are reported in a series of papers [44, 45, 52]. Firstly, there is the static contact angle measurement which designates an angle somewhere between θ_R (receding contact angle) and θ_A (advancing contact angle) and, secondly, the dynamic contact angle measurement which is when the substrate is tilted to a certain angle and the water droplets are made to move on such a tilted surface. The receding contact angle (θ_R) is the angle formed when a droplet on a surface is allowed to evaporate in a low humidity environment or if with a syringe the water is carefully withdrawn from the droplet, the droplet will decrease in volume and contact angle, maintaining the same contact area with the surface until it begins to recede (figure 10 a)) [45, 52].

In case of the advancing contact angle (θ_A) the droplet starts to increase the volume, the contact angle increases and the droplet begins to advance when the surface is cooled to below the dew point and water condenses on the droplet, or if with a syringe the water is carefully added (figure 10 b)). Hysteresis is the difference between the advancing and receding contact angles [45, 52].

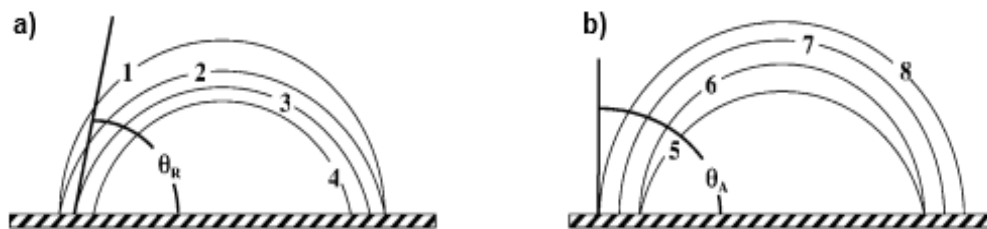


Figure 10 - a) Receding contact angle (θ_R) and b) Advancing contact angle (θ_A) [52].

The surface water repellence is dependent on the surface roughness and low surface energy of hydrophobic materials. In order to understand this dependency, it was found an explanation through two models, designated as Cassie-Baxter and Wenzel (figure 11) [45].

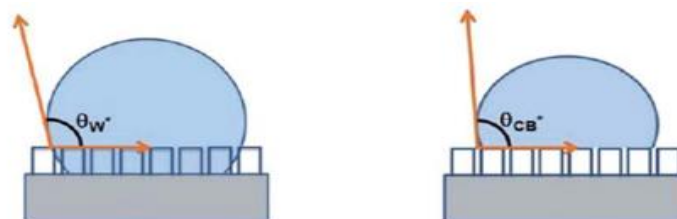


Figure 11 - Schematic diagram representing the water droplets on Wenzel model (left) and Cassie-Baxter model (right) [46].

Wenzel model shows that the liquid keeps intimate contact with a microstructure surface in which the change of the contact angle follows the equation (2) [46, 47]:

$$\cos \theta_w = r \cos \theta \quad (2)$$

The $\cos \theta_w$ is the Wenzel contact angle on the rough surface and r is the surface roughness factor (ratio between the true surface area over the apparent one). When water droplets penetrate into surface cavities the surface roughness factor tends to be greater than unity, which increases the contact angle in hydrophobic surfaces ($\theta > 90^\circ$) and decreases it in hydrophilic surfaces ($\theta < 90^\circ$). Thus, surface roughness leads to an amplification of the wetting properties of the smooth material [45, 53].

The Wenzel model is not valid for high roughness or porous structures and here the Cassie-Baxter model can be applied. This is when the absolute value of the right side from equation (2) is larger than 1. The Cassie model explains the effect of chemical heterogeneous wetting state which is when it is present an equilibrium contact angle. The air pockets are blocked underneath the water in the surface and for that reason liquid and solid contact area will be reduced and the reverse will happen between water and air (maximized). A composite state is present in this situation which means that the “air” parts of the surface can be considered perfectly non-wetting [45].

Take into account these conditions, a lower hysteresis will be formed and resulting in the formation of spherical droplets, with higher contact angles. Hysteresis may increase or decrease in the opposite direction of the surface roughness, so if hysteresis decreases surface roughness increases and hydrophobicity also increases [46, 54]. The Cassie model is described by equation (3) [53]:


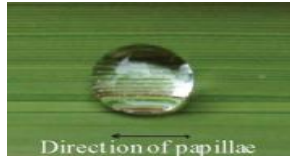


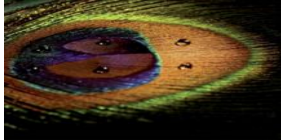

$$\cos \theta_c = f_s \cos \theta_s + f_v \cos \theta_v \quad (3)$$

Where f_s and f_v are the area fractions of the solid and vapour on the surface; θ_c is the Cassie-Baxter contact angle [53].

Since the late 20th century, the self-cleaning technology had evolved and achieved many breakthroughs ever since. Self-cleaning surfaces are commonly found in nature and most of the technologies created now intend to create bioinspired surfaces.

The most studied superhydrophobic coatings with self-cleaning properties are bioinspired surfaces in different animals and plants. Some of the bioinspired surfaces in nature are presented in Table 8 [53].

Table 8 - Overview of biomimetic self-cleaning surfaces present in nature (Adapted from [46, 53, 54]).

Bioinspired self-cleaning surfaces			
	Biological Topics	Properties of bioinspired surfaces	Pictures representation
Superhydrophobic surface	Lotus leaf	Superhydrophobicity	a) 
		Low adhesion	
		Low drag	
	Rice leaf	Superhydrophobicity	b) 
		Anisotropic wetting	
		Low drag	
	Cicada wing	Superhydrophobicity	c) 
		Anti-reflection	
	Butterfly Wing	Superhydrophobicity	d) 
		Directional adhesion	
Low drag			
Other examples:			
e) Peacock feather		f) Water strider	
			

Lotus effect present in lotus leaf is the first and the most well-known self-cleaning phenomenon in nature. Ward *et al.* was the scientist which observed that despite the lotus leaf rises from muddy water, it remains without any dirt and pollutants. Only after the invention of Scanning Electron Microscope in mid 1960s it was possible to study the lotus leaf surface and it was possible to observe a smooth surface with roughness on different scale lengths and epicuticular wax crystalloids, which makes the leaves superhydrophobic. Guo *et al.* divided the surface microstructures into hierarchical micro and nanostructures and unitary micro-line structures. During these studies was possible to verify that a self-cleaning surface is defined by two major important factors: the surface geometrical microstructures and low surface free energy [5].

Afterwards, was possible to divide these surfaces into four different surfaces as displayed in figure 12 [54, 55]:

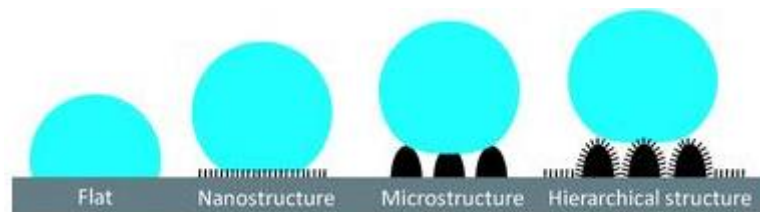


Figure 12 - Wetting of four different surfaces. The contact area is reduced in nanostructures surfaces and minimized in hierarchical structured surfaces [54].

In 1997, *Barthlott* and *Neinhuis* showed that the self-cleaning property of lotus leaves was due to their specialized surface morphology and high hydrophobicity. In case of the specialized surface morphology it prevents dirt from forming an intimate contact with the surface (low wettability) – self-cleaning property - and the high hydrophobicity makes leaf water repellent [46].

Measurements made by *Koch et al.* (2009) shown that the contact angle (CA) from a lotus leaf is 164° and the contact angle hysteresis (CAH) is 3° which is superhydrophobic and has self-cleaning properties. The water droplet on the leaf is almost spherical in shape and can roll easily with small sliding angles [46].

Other singularities were found in plants and insects. Anisotropic wetting surfaces are a characteristic from rice leaves, pigeon feathers, goose feathers, bamboo leaves and legs of some insects. Lotus leaf is isotropic which means it has the opposite characteristic from anisotropic. Anisotropic means that the surface shows different contact angles, roughness geometry and chemical heterogeneity measured in different directions. Along the papillae surface from rice leaves the water droplets roll off more easily along the direction of the rice leaf edge compared to the perpendicular direction. This unique property can be applied in microfluidic devices and evaporation-driven formation of patterns. It is also possible to modify synthetically the wettability from hydrophilic to superhydrophobic only by changing a structural parameter (without any chemical composition modified) to mimic this natural phenomenon [46, 53].

Many other biological characteristics supported the research and development of new technologies and advanced materials, however it is important to mention that biostructures have inspired coatings to be used in solar cells. Cicada wings and moth eyes microstructures were used as natural templates due to the antireflective properties which allow to transmit almost all the light incident on glass modules for photovoltaic applications [53].

The combination of superhydrophobicity and antireflection is very attractive, and inspired the production of multifunctional coatings. In order to satisfy both properties it is very important to control the surface roughness. Cicada wings can effectively remove dust and dirt particles from the wing surfaces, thus displaying self-cleaning properties, due to the periodic arrays of ncp nanopillars in the wings surface. *Yang et al.* mimicked these properties by a simple method to obtain a multifunctional coating [46, 53].

Superhydrophobic surfaces have been prepared with both organic and inorganic materials. In case of polymeric materials which are hydrophobic, the surface roughness control is really important. For inorganic materials which are usually hydrophilic after the fabrication there is the need to perform a surface hydrophobic treatment. Many scientists have created superhydrophobic surfaces through different ways and with different materials [49, 56].

A preparation of superhydrophobic coatings can be divided into two categories: making a rough surface from a low surface energy material and by modifying a rough surface with a material of low surface energy. To prepare rough surfaces it is possible to use different techniques such as: mechanical stretching, sol-gel processing, layer-by-layer assembly, etching, lithography, chemical and electrochemical depositions and chemical vapour deposition – Table 9 [5, 7].

Table 9 - Summary of methods to fabricate superhydrophobic coatings from various materials (Adapted from [5]).

Fabrication of self-cleaning coatings with superhydrophobicity			
Roughening the surface of low surface energy material		Making rough surface and modifying the surface with material of low surface energy	
Materials	Process	Materials	Process
Silicone(PDMS)	Etching/Casting	Polycrystalline metals(Al/Cu)	Etching
Fluorocarbons(Teflon)	Stretching/Casting	Composites(Au)	Lithography
Organic materials(PS+DMF)	Electrospinning	Polyelectrolyte+ Silica Nano particles	Layer-by-layer and colloidal assembly
Inorganic materials(ZnO)	Two step method	Alkoxysilane	Sol-gel processing

The sol-gel process has several advantages, such as: is applicable on an industrial scale, economic due to the reduced use of equipment, efficient, compatible with all solid substrates, easy to produce coatings and is possible to control the stoichiometry and therefore innovated coatings can be obtained. In respect to the disadvantages, the curing step can promote shrinking volume which may cause formation of crackings and the reagents cost, exceptionally the price of the precursors which in some cases can be expensive. Sol-gel route has been widely used for synthesis of inorganic compounds through a chemical reaction. It is possible to fabricate superhydrophobic surfaces through this route and the roughness from the surface can be changed only by modifying the composition of the reaction mixture and the protocol followed. Rough surfaces can be produced based on variety of oxides, such as: silica, alumina and titanium. However, the silica coatings are the most used. The most common silica precursors are the silicon alkoxides tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) [57]. The sol-gel process can form flat surface coatings, xerogel coatings or aerogel coatings depending on the conditions of each one. Both xerogel and aerogel coatings present rough surfaces. The sol-gel method is composed of several reactions, which are based on the preparation of macromolecular network involving hydrolysis of metal alkoxide groups and after a condensation from the silanols [50]. Layer-by-layer is a method more often used for preparing multilayer thin films. This is a simple and cheap method, in which there is a sequential deposition on a substrate of layers formed from solutions with opposite charged compounds. It uses electrostatic interactions and covalent bonds to form multilayers. An advantage of this procedure is the possibility to achieve a high degree of molecular control over the film thickness and for this reason it is easy to fabricate finely controlled surface morphologies. Hydrophobicity increases with the number of layers [57]. Etching is another alternative technique to produce superhydrophobic coatings with rough surfaces. This technique is simple and efficient and can be chemical, plasma and laser etching. Silica surfaces are used to apply micro textures and they exhibited superhydrophobic behaviour with water contact angles of 174° [57].

Other approaches can be used for the fabrication of superhydrophobic surfaces, such as lithography techniques which creates micro- and nanopatterns, spraying nanoparticle suspensions onto substrates which a one-step, time-saving and low-cost preparation of superhydrophobic surfaces. Besides, electrospinning is used in polymeric materials and is a powerful, simple and practical one-step method to produce continuous ultrathin fibres with micrometre and sub-micrometre diameters. However, there are many other techniques such as hydrothermal synthesis, electrospinning, etc., which were developed all over the years and the research is ongoing as like in this thesis, contributing to innovative coatings with different compositions [5, 7].

2.3.2. Energy applications and benefit properties of superhydrophobic coatings

The superhydrophobic coating with self-cleaning properties elaborated in this Master Thesis is intended for photovoltaic solar cells applications. However, it is also important to mention that this type of coatings is present in many fields.

Recently, superhydrophobic surfaces have been developed in airplanes, wind turbines, electric power lines, photovoltaic cells, heat exchangers, ice slurry generators, microfluidic devices or microchannels and in most power generation industries. These surfaces avoid ice and snow accumulation due to severe conditions; therefore, less energy is consumed and stabilizes the working conditions from these devices [58]. Besides efficiency improvements, the coating can reduce the catastrophic risks of icing in airplanes by preventing ice formation or adhering into the surface. The frictional pressure losses of flow through the tubes can be reduced by using superhydrophobic coatings. Also, the surface wettability plays a key role by enhancing the boiling and condensation heat transfer performances. Although, other applications exist for superhydrophobic surfaces, the main properties looked for are anti-adhesion, friction reduction, anti-icing and anti-frosting. However, many more are being developed, such as the self-cleaning property, anti-biofouling in wave energy devices and all kind of underwater structures. Furthermore, the concept of preparing surfaces which repel water creates huge opportunities in the area of corrosion protection of metals and alloys that are used for example to manufacture the tubes and heat exchangers. The metallic substrates with superhydrophobic coatings could effectively prevent corrosion because the air trapped in the cavities could separate the liquids from the surfaces. Moreover, the durability is also important to all practical applications because the coating determines the performance of the devices in the long-term operation [7, 58, 59].

3. Experimental methods

This chapter addresses the fundamentals of the sol-gel process, the deposition methods and describes the final steps to achieve the final coating. Furthermore, the characterization techniques will be explained.

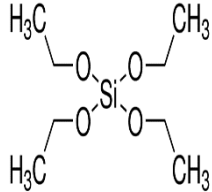
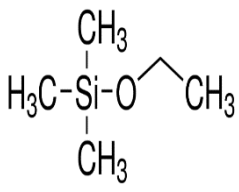
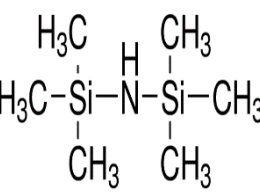
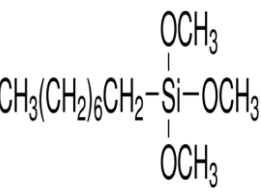
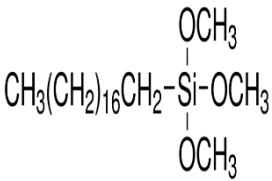
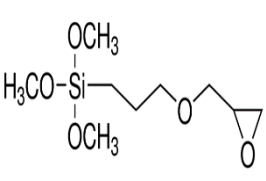
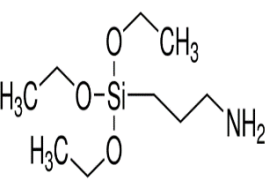
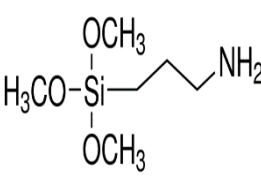
3.1 Sol-gel route

3.1.1. Precursors

In order to prepare a colloid there is the need of a starting compound which consists of a metal or metalloid element surrounded by various ligands and it has high solubility in organic solvents. A sol-gel coating is commonly composed by tetraalkoxysilanes or organoalkoxysilanes. The most used tetraalkoxysilanes are tetraethoxysilane, TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and tetramethoxysilane, TMOS ($\text{Si}(\text{OCH}_3)_4$). There is also other type of silanes named of organoalkoxysilanes ($\text{R}'\text{Si}(\text{OR})_3$). The type of precursors used are composed with an alkoxy group due to the ligand formed by removing a proton from the hydroxyl in an alcohol, as methoxy ($-\text{OCH}_3$) or ethoxy ($-\text{OC}_2\text{H}_5$) and silanes which in general have the following formula $-\text{Si}_n\text{H}_{2n+2}$ – in case of a linear structure [60].

Some examples of organoalkoxysilanes are: trimethylethoxysilane (TMES), trimethoxy(octyl)silane (TMOOS), trimethoxy(octadecyl)silane (TMODS), (3-Glycidyloxypropyl)trimethoxysilane (GPTMS), 3-aminopropyl)trimethoxysilane (APTMS) and (3-aminopropyl)triethoxysilane (APTES). In case of hexamethyldisilazane (HMDS) the precursor is called of organoalkylsilane. An alkyl is a ligand formed by removing one hydrogen (proton) from an alkane molecule producing methyl ($-\text{CH}_3$) or ethyl ($-\text{C}_2\text{H}_5$) [60]. The table 10 shows the precursors used in this master thesis.

Table 10 - The precursors used in the experimental work were: TEOS(98%), TMES(98%), HMDS(99%), TMOOS(96%), TMODS(90%), GPTMS(98%), APTES(99%) and APTMS(97%). All the silanes were purchased from Sigma-Aldrich.

Precursors			
TEOS	TMES	HMDS	TMOOS
			
TMODS	GPTMS	APTES	APTMS
			

All the precursors were chosen due to the peculiarities of the chemical structure. According to the literature, superhydrophobic coatings were obtained previously with the following silanes used: TMES, HMDS and combination of TEOS with other precursor [49, 61]. TEOS is commonly used in the sol-gel process because it readily reacts as precursor, promotes formation of cross-linking and has networker characteristics. Other precursors were used with different organic groups, such as: TMES and HMDS which are hydrophobic silanes due to the methyl group which is strongly hydrophobic and the hydrolysable groups are ethoxy and silazane group(-NH) respectively, TMOOS and TMOOS due to the long n-alkyl chain length which promotes strong hydrophobic links, GPTMS due to the epoxy ring which promotes the durability of the coating and APTES/APTMS due to the amine groups which promote adhesion of the coating to the substrate.

3.1.2. Catalyst, solvent, pH and H₂O:Si molar ratio (r') dependence

The four parameters which are inter-related and influence the following steps of the sol-gel process are: H₂O: Si molar ratio(r'), pH, catalyst and solvent. The reactions which start after mixing the components have a different behaviour in case of a basic or acid solution. Hence, before starting the experimental work is important to define what we want to obtain and chose the best conditions to achieve our target. It is also important to select a pH range which prevents precipitation in order to avoid reduced silica concentration. According to figure 13, the range of pH's which achieves stable sols are approximately between 6.5 and 10.5 [60].

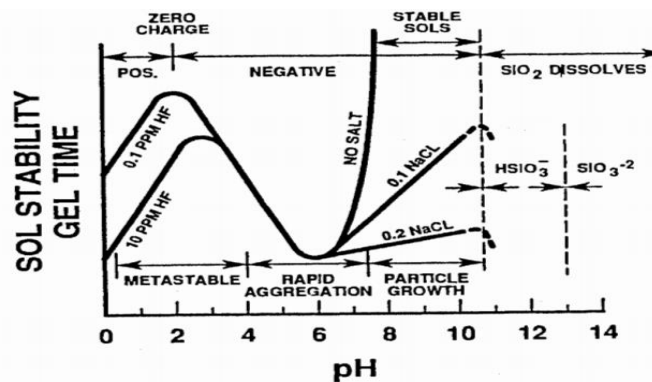


Figure 13 - Sol stability versus pH [60, 62].

The SiO₂ dissolves if the pH is above 10.5; between 6.5 and 10.5 there is a particle growth in size with decrease in number; between 4 and 6.5, or in the presence of flocculating salts, there is a rapid aggregation of particles (linking of particles into chains, then three dimensional networks which extend throughout the liquid medium, thickening it to a gel). Below 4 there is a metastable state, which means the system spends an extended time in a configuration rather than the system's state of least energy. The pH values selected in the laboratorial work were between 6.5 and 10.5 and the best result was achieved with pH equal to 6.5. In this interval usually particles are ionized so that growth occurs without aggregation or gelation. A schematic representation of the polymerization behaviour in relation to the selected pH is presented in the figure 14 [60].

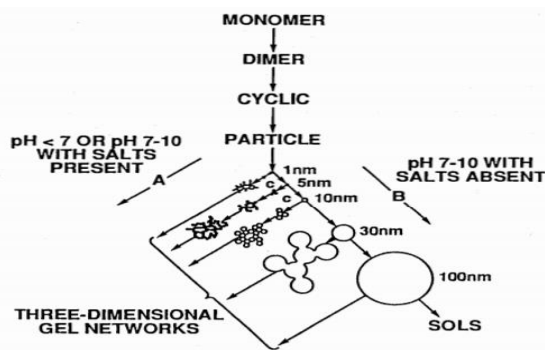


Figure 14 - Polymerization behaviour of aqueous silica [60, 62].

The strength and concentration of a basic and acid catalyst accelerates and extends the process of hydrolysis. The acetic acid and the ammonium hydroxide base are examples of some widely used catalysts. In case of weaker acids such as acetic acid, they require longer reaction time to achieve the same extended reaction. Acidic conditions are more dependent of the nature of the solvent. In basic conditions the hydrolysis kinetics are more affected by the nature of the solvent compared to acidic conditions. The most used catalyst in the experimental work was ammonium hydroxide which is a weaker base (Table 11). The catalysts, when they are weaker bases, are dependent on their concentrations and measurable reactions rates are only possible for large concentrations of the catalyst [60, 62, 63].

To form a sol – a colloidal suspension of solid particles in a liquid - is essential to add a mutual solvent which works as a homogenising agent, because TEOS and water are immiscible. A solvent is also added to prevent liquid-liquid phase separation during the initial stages of the hydrolysis reaction. The main characteristics of a solvent are: polarity, dipole moment and availability of labile protons. Solvents can be polar, nonpolar, protic (containing a removable or “labile” proton) and aprotic. Some examples of protic solvents are: water, methanol, ethanol, etc. The availability of labile protons influences the extent of reverse reactions in the sol-gel process, named as esterification and alcoholysis reactions [60, 62, 63]. A variation of $H_2O:Si$ molar ratio (r') also influences the sol-gel process. An increased value of r is expected to promote a fully hydrolysed reaction (containing a large amount of $\equiv Si-OH$ groups) and causes liquid-liquid immiscibility [60, 62, 63].

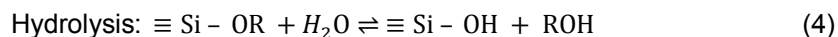
Table 11 - Solvents and catalysts used.

Solvent	Methanol(MeOH, 99,9% Merck), i-prop (Sigma-Aldrich) or Ethanol(EtOH, 99,9% Merck);
Catalyst	Solution of NH_4OH 2M or Pure water(H_2O Millipore)

3.1.3. Hydrolysis and condensation

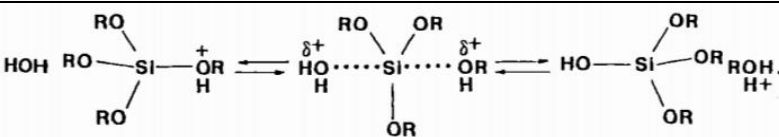
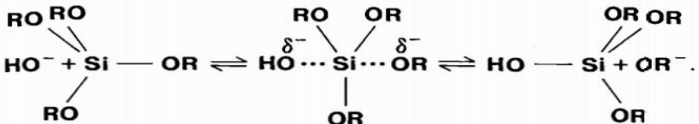
The structure of sol-gel coatings evolves sequentially as the product of successive hydrolysis and condensation reactions. Firstly, there is the hydrolysis, which consists of a replacement of alkoxide groups (OR) with hydroxyl groups (OH) - R and R represents an alkyl group (equation (4)). Secondly, the condensation reactions consist on the polymerization to form the siloxane bonds (functional group

in organosilicon chemistry with the Si-O-Si linkage) which occurs either by an alcohol or water condensation reaction (equation (5) and (6) respectively). The polymerization is the process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks [60].



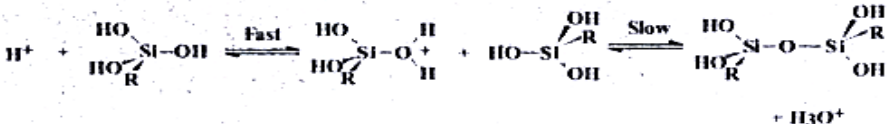
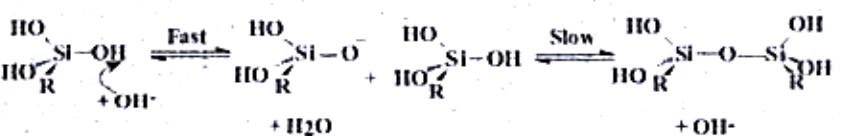
Hydrolysis and condensation occur by acid or based-catalyzed bimolecular nucleophilic substitution reactions ($\text{S}_{\text{N}}2$) (table 12 and 13). The reverse reaction of hydrolysis is esterification and from alcohol and water condensation is alcoholysis and hydrolysis respectively [60].

Table 12 - Mechanisms of hydrolysis [60].

Mechanisms of Hydrolysis	
Acid-catalyzed	
Base-catalyzed	

The condensation reactions proceeds via a rapid formation of a charged intermediate by reaction with a proton or hydroxide ion, followed by the slow attack of a second neutral silicon species (table 13) [64].

Table 13 - Mechanisms of condensation [64].

Mechanisms of Condensation	
Acid-catalyzed	
Base-catalyzed	

3.1.4. Silica Nanoparticles Modification

A comparison between a sol-gel coating unmodified and modified with SiO₂ nanoparticles (SNPs) from WACKER (HDK®H2000) was made. The silica nanoparticles from WACKER are synthetic, hydrophobic, composed with amorphous silica and were produced via flame hydrolysis. The data from the silica nanoparticles characteristics and physical-chemical properties are presented on Table 14. In the literature several superhydrophobic coatings have been prepared through sol-gel route and modified with SNPs, such as: Lin *et al.* (2013) [6], Kumar *et al.* (2015) [10], Deng *et al.* (2014) [11], Wang *et al.* (2011) [48], Xu *et al.* (2014) [51] and Xiu *et al.* (2008) [56].

In the beginning, a low weight percentage of SNPs (between 0.1% and 0.6 %) was used and superhydrophobicity was not achieved. Moreover, a higher weight percentage of SNPs was used - 1% - and superhydrophobicity was reached. So, the contact angles increase with increasing filler content of SNPs. This occurs because it is formed a clustering of the silica nanoparticles on the surface which leads to a highly hierarchical rough surface [11].

Table 14 General characteristics and physical-chemical properties from WACKER(HDK®2000) silica nanoparticles.

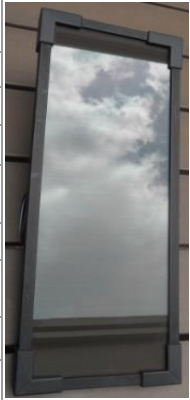
Product data from WACKER (HDK®H2000)			
Characteristics		Physical-chemical properties	
Density at 20°C (SiO ₂)	Approx. 2,2 g/cm ³	Carbon content	2,3-3,2 %
Residual silanol content (relative silanol content in relation to the hydrophilic silica, which shows approx. 2 SiOH/nm ²)	25%	pH – Value in 4% dispersion (1:1 mixture of water-methanol)	6,5-8,0
BET surface area of hydrophilic silica	Approx. 200 m ² /g	Tamped density	100-250 g/l
INCI name	Silica Silylate	Loss on drying (2h at 105°C)	<0,6 %
		Surface modification	Trimethylsiloxy

3.1.5. Substrates preparation and coating application

The substrates used in the experimental work were:

- Glass slides (KING, 26 mmx76 mm);
- Carbon steel;
- Commercialized solar panels (characteristics are presented in the table 15) [65];
- Organic solar cells (OPVs) produced in the research laboratory of Institute of Telecommunications which were used for efficiency evaluation – Figure 15 d);

Table 15 - Solar panel characteristics [65].

Solar panel characteristics		
Technology	a-Si (amorphous silicon) Thin film	
Surface constitution	Tempered glass/ITO(indium tin oxide)	
Maximum power (P_{max})	2.5 W	
Voltage	12 V	
Open circuit voltage(V_{oc})	21.5 V	
Maximum charging current(I_{mp})	167 mA	
Range of temperature	-40°/+80°C	
Module dimensions(LxWxH)	325x125x22 mm	
Weight	0.45 kg	
Brand	Xunzel	

The pre-treatment of the substrates before the coating application was:

- Glass (figure 15 a)) – Ultrasonic bath for 15 minutes with ethanol and then the surface was dried with the dryer.
- Carbon steel (figure 15 b)) – Polished with paper grit of silicon carbide (SiC) with different granulometries of 180, 400 and 800 (Struers, LaboPol-25), after ultrasonic bath for 15 minutes with ethanol and then the surface was dried with the dryer.
- Solar panel (figure 15 c)) – without any pre-treatment and with ultrasonic bath for 15 minutes with ethanol and then the surface was dried with the dryer.

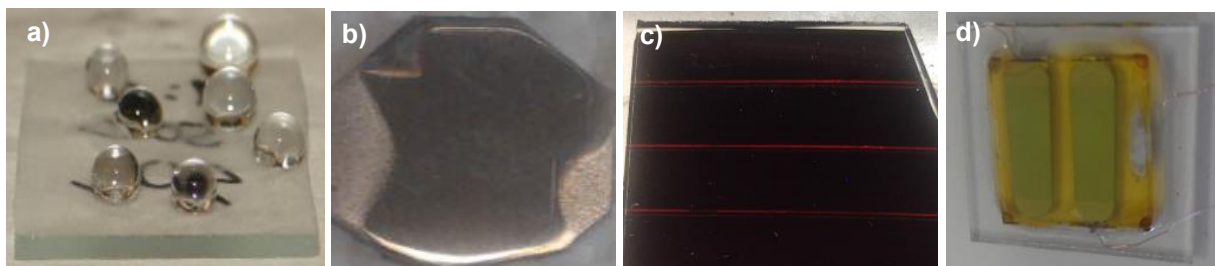


Figure 15 - a) Glass surface; b) carbon steel surface; c) solar panel surface [65] and d) glass encapsulated organic solar cell (OPV) only used for efficiency evaluation.

The following deposition processes were selected depending on several factors: the same technique must be compatible with glass and carbon steel substrates; possibility to apply into PV solar panels industry; provide good adhesion of the coating to the substrate; maintain the same properties with different PV solar panels sizes; to have a low price, flexibility concerning size and shape; to be easy to apply and intuitive; equipment required and availability of the same. The most common deposition processes fulfilling these requirements are dip-coating and spray coating [66]. Dip-coating technique can be applied during production of PV solar panels and spray coating can be applied during panel production and also to already installed PV solar panels.

3.1.6. Dip-coating

Dip-coating or the immersion technique consists on the application of the sol into the substrate by immersing the substrate into de solution in one single step or in sequential steps. This technique can be divided into five stages: immersion, ascending, deposition, drainage and evaporation [60] - figure 16 – and the equipment used is presented on Figure 17.

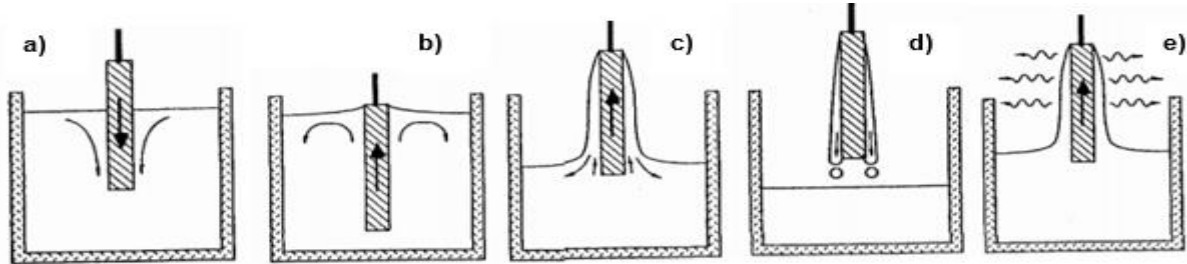


Figure 16 - Steps of dip-coating technique: a) immersion; b) ascending; c) deposition; d) drainage; e) evaporation, adapted from [60].

The parameters which were controlled during this technique were:

- 1) *Immersion time*: in the first experiences, time of immersion was changed to assess its effect. It was possible to conclude that changes with time were not relevant and for that reason the following experimental attempts were with 10 seconds of immersion time each.
- 2) *Withdrawal speed*: can vary between 4 cm/min and 40 cm/min. The faster withdrawal speed results in a thicker coating layer. The prepared sol-gel coating was applied on glass slides with speeds of 16 cm/min.
- 3) *Number of immersions*: the number of sequential immersions was increased from 1 to 3 times. The number of immersions increases the thickness of the coating.

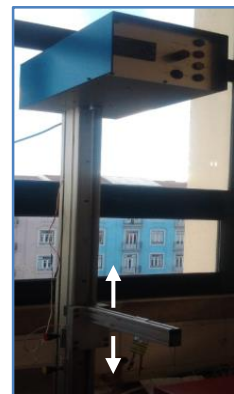


Figure 17 - Equipment used for dip-coating (Siemens Logo! 12/24RC model).

The dip-coating technique besides being fast and of facile application also has the advantage of an equal distribution of the coating along the substrate which sometimes is not easily obtained by other application techniques.

3.1.7. Spray coating

Another technique to apply the sol into the substrates is to spray the coating into the samples – glass slides, carbon steel and solar panel surfaces. This technique was made with a conventional hand trigger sprayer (KB-1003, 300 mL) and needs careful handling to obtain an equal distribution of the coating throughout the surface. It is important to highlight that the same place sometimes will need to

be sprayed more than once due to the amount of sol liberated by the sprayer each time. The main advantage of this technique is that there is no need for an expensive equipment and is accessible to any person. It is also really easy to apply a spray to any surface and in this case to PV solar panels. Despite the benefits, there is a disadvantage of the spray operation which is the low transfer efficiency which means that exists a difference between the amount of material which adheres to the substrate compared to the amount of material which was sprayed by the applicator toward the substrate due to losses of material throughout the atmosphere [66].

3.1.8. Curing

Drying is the final step of the sol-gel process. During drying the solvent is evaporated from the interconnected pore network. In this step, is possible to choose between different temperature conditions (at room temperature (RT) or fix the temperature and time in the oven). By experimental trials it was possible to observe better results with higher curing temperatures. However, the final coating gives good results, independently of this factor. The main problem of drying is the large capillary stresses which can be developed when the pores are small ($< 20\text{nm}$). While the body shrinks, it promotes the formation of cracks. The cracking problem can be controlled in the presence of a low surface energy (characteristic of a superhydrophobic surface) or by addition of surfactants. Surfactants reduce the shrinkage at the critical point by reducing the interfacial energy. The risk of fracture during the process of drying can be diminished by aging (rate of condensation is accelerated and there is a lower bulk density) a gel before drying, because helps strengthen the network. After the body shrinks, it becomes too stiff to shrink and the liquid recedes into the interior, leaving air-filled pores near the surface [60, 67].

3.2. Characterization techniques

In the following subchapter are going to be presented the characterization techniques used to study the unique coating produced, which were:

- Measuring the static water contact angles in a Goniometer by Sessile Drop Method in order to determine if is achieved superhydrophobicity;
- Observation of the surface structure by optical microscopy;
- Characterization of the coatings morphology through Scanning Electron Microscopy (SEM);
- Transmittance measurements with a UV/Vis Spectrometer to know if the coating affects substantially the absorption of light in glass substrates;
- Comparison of two organic solar cells efficiency without coating and with the best coating modified and unmodified;

3.2.1. Contact angle measurements

The wettability of the dried substrates was determined using the Sessile drop method. In each sample, three drops of Millipore water (extremely pure water) were generated with a micrometric syringe and deposited in three different locations of the substrate surface during 1 min each. The sample was placed inside a thermostatic-controlled ambient chamber model 100-07-00 (Ramé-Hart, NJ, USA). In cases which the sample overpassed 50x36 mm, the chamber could not be used. The images of drops were obtained through a video camera (jAi CV-A50, Spain) mounted on a microscope Wild M3Z (Leica Microsystems, Germany) and they were examined by running the ADSA (Axisymmetric Drop Shape Analysis, Applied Surface Thermodynamics Research Associates, Toronto, Canada) software. The equipment used to perform the wettability test is called Goniometer (Figure 18).

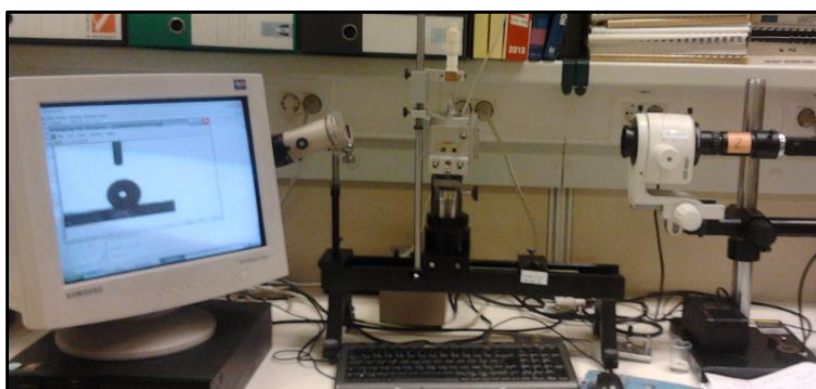


Figure 18 - Goniometer used for the wettability measurements.

The Sessile Drop method was used to determine the static contact angle measurements. This method is based on the concept explained in figure 9 and in the sub-chapter 2.3.1. – Superhydrophobic coating with self-cleaning properties. Basically, the wettability of the surface can be characterized by the contact angle (CA). The contact angle (θ) is defined as the angle which the droplet or edge of the liquid makes with the solid plane (figure 8) [68]. Through this method is only possible to measure the static contact angle which is when the droplet is standing on the surface and the three phase boundary is not moving [52]. In this experimental work it is intended to obtain a superhydrophobic coating and through this method it is possible to evaluate if the CA is higher than 150° or not. Although, in the best coating, without moving the three phase boundary and within a horizontal plan, it was possible to see that in the majority of the surface the droplet was moving away. Despite the sessile drop method is not able to measure the dynamic contact angle (when the three-phase boundary is moving), it was possible to visualize that with almost any sliding angle the droplet rolls-off. When this happens it can be proposed that the surface shows self-cleaning properties (Figure 19).

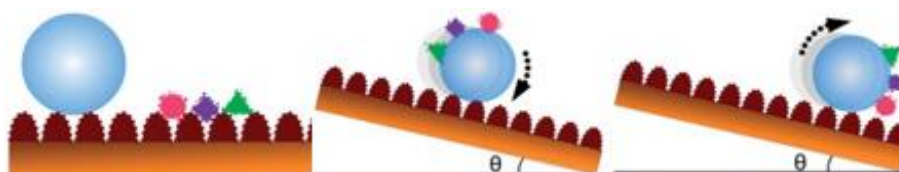


Figure 19 - Schematic of a superhydrophobic coating ($CA > 150^\circ$) with self-cleaning properties (sliding angle and contact angle hysteresis (CAH) lower than 10°) [8].

The self-cleaning property was tested by applying droplets with a micrometric syringe into the substrate. The property was always observed for droplets with different sizes, when were applied either fast or slow onto the surface and with different distances from the substrate. Besides, the PV solar cell, glass or steel substrates were placed inside the thermostatic-controlled ambient chamber from the goniometer without or with a slightest inclination and in a completely flat surface from the laboratory and the behavior was kept constant in different conditions and substrates.

3.2.2. Optical microscope

An optical microscope (Leica DM 2700) was used to visualize in detail the morphology of the surface. The apparatus generates the final digital images of each sample and for that the microscope needs to be adjusted to achieve the best focus, magnification, resolution, contrast and working distance. Optical imaging is obtained by an image forming by a lens system. Through convex lens and light, the process of refraction occurs and a diverging spherical wave of light is radiated. The point spread function (psf) is the smallest possible size if the system is in focus [69]. The magnification is when the point source moves away from the origin to a new position and it was set with 10x, 20x and 50x.

3.2.3. Scanning Electron Microscope (SEM)

The scanning electron microscope (FEG-SEM, JEOL JSM-7001F) was used to obtain micrographs of higher resolution. The SEM can also be used to obtain three-dimensional images which help at obtaining a better morphological characterization. The area to be examined is irradiated with a finely focused electron beam. For that reason, before placing the samples into the microscope is necessary to have a conductive surface. In case of the glass substrate it was covered with a thin layer of gold. The voltage applied to the beam was 15 or 20 kV. The two major components of SEM are the electron column and the control console [70]. Figure 20 a) represents a scheme with a complete description of the system and Figure 20 b) shows the SEM used.

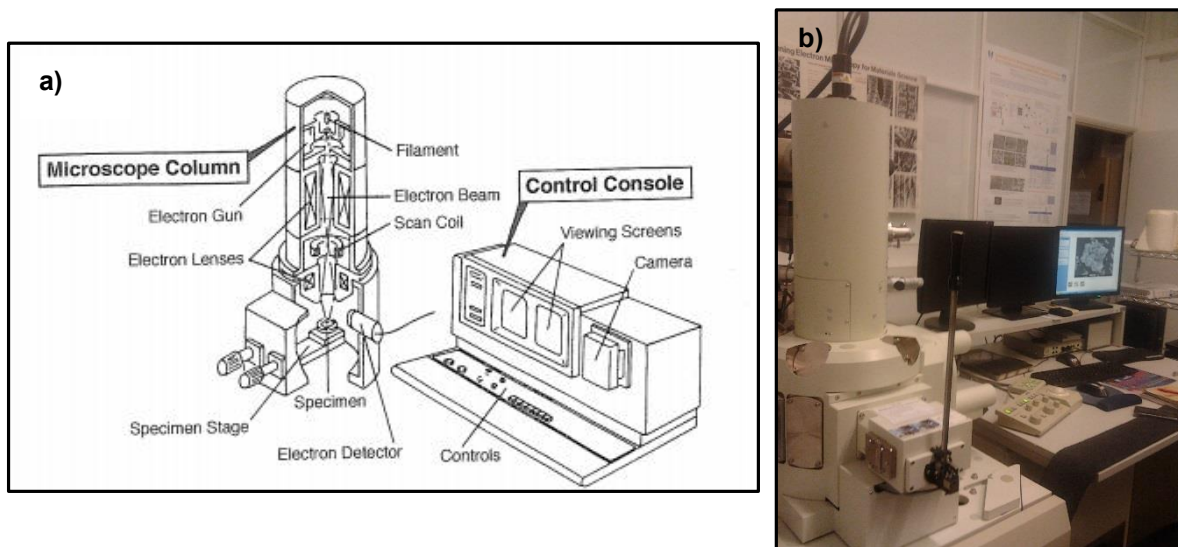


Figure 20 - Scheme of the scanning electron microscope components (a)) [70] and the equipment used (b)).

3.2.4 Transmittance measurements

Another important characteristic which should be studied is the transparency of the coating. Anti-reflective properties of the coating should be investigated to know if it can be applied or not in the PV solar cells industry. In case the reflection is almost none the coating is anti-reflective and the transmittance is approximately 100%. Transmittance is defined as the fraction of incident light which passes through a sample with a specific wavelength. When a coating is applied to a substrate the transmittance may increase or decrease, depending on the surface roughness, film thickness and refractive index. In most of the cases, transmittance decreases with increasing roughness [71].

The transmission measurements were made by using a UV/Vis Spectrometer (PerkinElmer, Lambda 35) – Figure 21 - with an ultraviolet-visible spectral region set between 300–700 nm. The plots obtained were Absorbance (A) versus wavelength (λ) and is intended to study the percentage of transmission (%T) versus wavelength (λ).

In order to transform Absorbance into percentage of transmission, were made the following computations [71]:

$$A = -\log T \quad (7)$$

$$A = 2 - \log(\%T) \quad (8)$$

Equation (7) gives the transmittance (T) and equation (8) the percentage of transmission (%T) [71]. When the percentage of transmission is higher the transparency is also higher. The study was done using glass slides as substrate over which the best coating was applied. A comparison was performed between the transmittance percentage (%T) of a simple TMES sol-gel coating and a TMES sol-gel modified with silica nanoparticles (SNPs).



Figure 21 - UV/Vis Spectrometer (PerkinElmer, Lambda 35).

3.2.5. Solar cells efficiency evaluation

Measuring efficiency is of utmost importance in photovoltaic solar cells. Through these measurements it is possible to calculate the ability of the solar cell to convert sunlight into usable energy. In this step it is intended to study how the application of the coating onto solar cells surface affects the performance parameters of the solar cell. The parameters are: open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF) and efficiency (η). To compute the efficiency is necessary to calculate first the other performance parameters. The intersection with the voltage axis, which corresponds to “no current”, is denominated as open-circuit voltage and when the intersection is in the current axis, and there is no application of any external potential (when $V=0$), is denominated as the short-circuit current. In order to obtain the current in a specific area of the solar cell the current was converted into current density (J) – mA/cm². The fill factor is the ratio between maximum power (P_{max}) generated by the solar cell and the product of open-circuit voltage and short-circuit current - equation (9). The maximum electrical power delivered by the cell is achieved when the voltage and the current density have the highest values. After obtaining these parameters is possible to compute the efficiency of the solar cell through the maximum power generated by the solar cell divided by the incident radiant energy – equation (10). The standard test conditions (STC) were used which means the incident radiation flux (P_{in}) is 1000 W/m² [72].

$$FF = \frac{P_{max}}{V_{oc} I_{sc}} \quad (9)$$

$$\eta = \frac{I_{sc} V_{oc} FF}{P_{in}} = \frac{(JV)_{max}}{P_{in}} = \frac{P_{max}}{P_{in}} \quad (10)$$

The typical J-V curve for a solar cell is given by the Figure 22 [72].

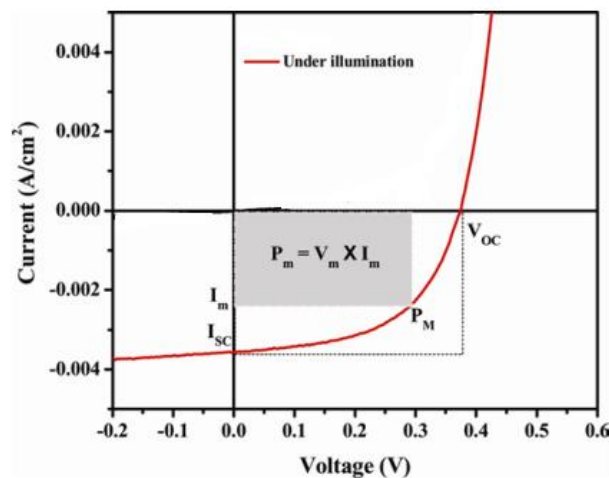


Figure 22 - Typical J-V curve for a solar cell (Adapted from [72]).

The measurements were made when the coating was applied onto organic solar cells kindly provided by Prof. J. Morgado from the Institute of Telecommunications. Organic solar cells have been a highlight in research due to the low fabrication costs, low weight which is easier to install and can be produced in substrates with large areas [72]. The efficiency of a commercial solar panel (as used to measure the contact angles) could not be measured with the available equipment because the solar panel had a large area and capacity, which did not allow to do the measurements. For that reason, this test was performed by applying the coating onto organic solar cells with small dimensions. The organic solar cells were encapsulated with glass and the coating was applied into the glass substrate (the surface was very similar to all the others tested) – Figure 23.

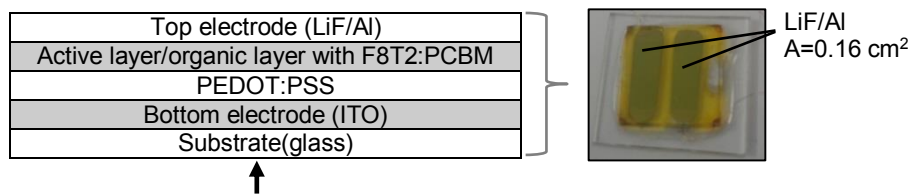


Figure 23 - Structure and picture of the organic solar cell used.

The first step was the measurement of the current as a function of the applied voltage - between -1 and 1.5 V. The applied voltage was controlled with a source voltage and a current meter *Keithley* 2400. It was used a solar simulator AM 1.5 G from *Newport* brand and model *Oriel*, SOL 3A™ as source of illumination and with a lamp power of 100 mW/cm². The measurements were controlled with a computer which allows to obtain the generated current values by a solar cell with an applied voltage. The illuminated I-V measurements were made with a Xenon lamp and a monochromator which enabled to measure the current in function of the wavelength – $\lambda=300$ nm. The data obtained allowed to compute the performance parameters (V_{oc} , J_{sc} , FF and η). The equipment used is presented in Figure 24.

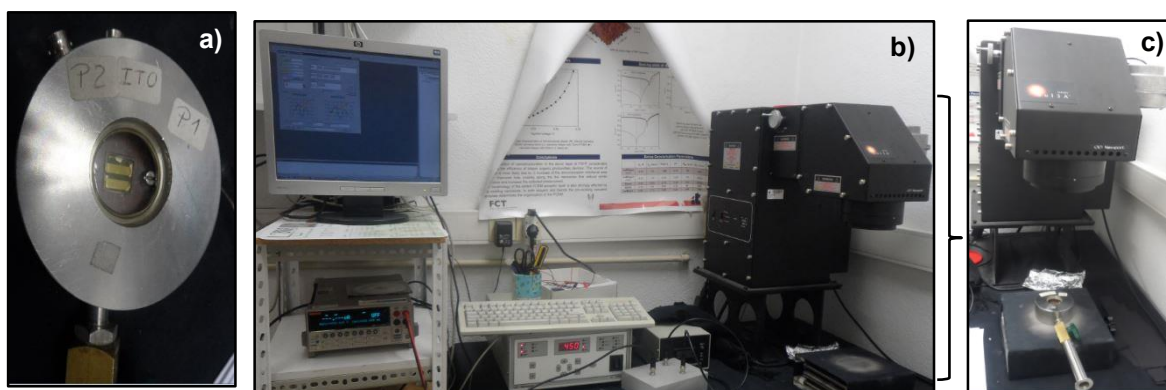


Figure 24 - a) Measurement cell; b) Set-up from the equipment used for measurement of electrical characteristics; c) Solar simulator.

4. Results and discussion

4.1. Overview of the experimental results

An overview of the 19th sol-gel coatings produced are presented in the following subchapter - Table 16. The components used to elaborate the coatings were: a solvent, a basic catalyst and precursor(s). The solvents used were: methanol (MeOH), isopropanol (i-prop) and ethanol (EtOH). Methanol was used in the trial with TEOS as precursor and with the paper attempt with TMES as precursor. Isopropanol was used in the attempts made with GPTMS as precursor. Ethanol was selected for all the other attempts due to the improved results achieved in comparison to the other solvents.

In respect to the catalyst, it was possible to choose between two routes: basic or acid catalyst. The route chosen was a strong basic catalyst due to the use of silica alkoxides as precursors. It consisted of ammonium hydroxide (NH₄OH) 2M, which promotes rapid hydrolysis and condensation of alkoxide silanes and the formation of highly branched clusters, which enhance hydrophobicity. The ammonium hydroxide was the catalyst chosen because after some trials was obtained higher hydrophobicity with this catalyst in comparison to water. The acid-catalyzed route was not used because it resulted in weakly cross-linked linear polymers, which entangle and lead to gelation [73].

Another important component of the mixture was the precursor, which can be one or more. The precursors used were organoalkoxysilanes: APTES, GPTMS, APTMS, TMOOS, TMODS, TMES, HMDS and TEOS. The majority of the experimental attempts used two precursors: TEOS and other Si-alkoxide.

The conditions varied to obtain the intended superhydrophobic coating were: H₂O:Si:Solvent and Si:TEOS molar ratios composition, the pH, stirring time and speed, curing time and temperature and application techniques which were dip-coating and spray coating. These studies verified that it was necessary to follow a trial and error experimentation to achieve our goal. Varying molar ratios between TEOS and other silane were prepared and the results obtained in terms of hydrophobicity were not proportional. After some experiments it was possible to select the best conditions to meet the target.

The silanes which achieved better results were: TMOOS, HMDS and TMES. In case of TMOOS, was attained contact angles higher than 130° for both glass and steel substrates. Then, a superhydrophobic coating was achieved with contact angles above 153°. The coating was modified with silica nanoparticles and had only HMDS as precursor. The highest contact angle without modifying the coating with silica nanoparticles was obtained by combining HMDS and TEOS as precursors. This coating has a contact angle of 142° and a molar ratio between HMDS and TEOS equal to 1:2.

Afterwards, TMES precursor was used and the results obtained at pH equal to 6.5 were better than the results obtained at pH equal to 10. Superhydrophobicity was achieved with different molar ratios between TMES and TEOS, which were: 1:1, 1.1:1, 2:1, and 1:0 for pH = 6.5 and with molar ratios between TMES and TEOS of 1:2 and 1:0 for pH = 10. The contact angles obtained at pH = 6.5 varied between 154° and 158°. The coating displayed both superhydrophobicity and self-cleaning properties only used TMES as precursor and added 1 % of silica nanoparticles. Through experimental trials was

verified that when the weight percentage of SNPs increases the hydrophobicity increases too. However, only with the addition of silane precursors it was possible to obtain superhydrophobicity.

According to literature, the application of SiO₂ nanoparticles in coatings prepared via the sol-gel route has been proposed to enhance superhydrophobicity [51, 74]. Some of the advantages of adding silica nanoparticles are: improvement in low refractive index, thermal and chemical stability.

The majority of the attempts were inspired by the paper of Sanjay *et al.* [49] but the conditions were modified. This paper used methanol as solvent instead of ethanol and the chemistry formulation composition used in the paper was different from this work. The curing temperatures used in the experimental work were one third of the temperatures reported in the paper. The coating prepared in the paper was not modified and in this MSc thesis 1 % of silica nanoparticles was used to modify the TMES sol-gel coating. This paper was used as a reference not only for the tests with TMES precursor but also for the other precursors. In the paper was not mentioned the pH and in this work it was varied within the interval of stable sols (figure 13) until reach superhydrophobicity. The stirring time and speed were also different from the paper. In case of the stirring time it was increased from 20 min to 1 hour and the speed varied between 300 and 400 rpm at room temperature (RT).

The curing conditions initially selected were 150°C and 2h as mentioned in the Sanjay *et al.* [49] paper. However, the coating is to be applied onto PV solar panels industry which has usually a maximum operating temperature of 80°C. So, the temperatures used were reduced along the trials while increasing the time - 50°C and 20h. Although, with our conditions superhydrophobicity was achieved with contact angles higher than 155° and by repeating the paper conditions, the superhydrophobicity was not reached. In the paper [49] the conditions were: TMES:TEOS molar ratio 1.1:1, methanol as solvent, 20 min of stirring with 300/400 rpm and curing of 150°C during 2h and contact angles of 152° were achieved.

In summary, the optimized conditions used for the best coatings includes: ethanol as solvent, ammonium hydroxide as catalyst, one hour of stirring time, pH=6.5, curing of 50°C for 20h and a formulation which better fits to our experimental trials, which was: TEOS: EtOH: NH₄OH 2M equal to 10 mL of TEOS as calculation basis and EtOH: NH₄OH 2M always 15:3 volume ratio and a variation of Si: TEOS molar ratio. The coating which displays superhydrophobicity with self-cleaning properties has solely TMES as precursor and the molar ratio from H₂O:TMES:solvent was 3.78:1:5.78. Table 16 identifies the source from which the procedure was adopted which refers to the conditions applied in the paper Sanjay *et al.* [49] and Xiaoguang Li *et al.* [61] that uses TMES and HMDS as precursor, respectively. In case of the TMOOS precursor, at our best knowledge, it was not used before for the production of superhydrophobic coatings and for that reason the results of this MSc thesis provided a new original sol-gel formulation objective.

4.2. Experimental Setup

The conditions of each coating prepared through sol-gel route and respective hydrophobicity achieved, are presented on Table 16. Different variations were made, such as: precursors selected, water: precursor(s):solvent molar ratio formulation, molar ratios between precursors, pH which is of utmost

importance to obtain the desirable stable sol, application technique of the coating to the substrate, curing temperature and time. Each step from the preparation of the coating was done consecutively. Since the stirring of the solution mixture until the characterization of the coating with contact angle measurements.

Table 16 - A glance table from the experimental work.

Si (Silanes)	Molar Ratios		pH	Application	Curing (oven humidity=60%)	Hydrophobicity	
	H ₂ O: Si+TEOS: solvent	Si:TEOS					
TEOS	1:1:4	—	10	Dip-coating	200°C/30 min	Hydrophilic	● ○
	8.67:1:38.44		8.1	Dip-coating	150°C/2h	Hydrophilic	● ○
	2:1:13		8	Dip-coating	150°C/2h	Hydrophobic	●
	3.78:1:5.78		6.5	Spray	50°C/20h	Hydrophobic	●
APTES	0.1:1:0.9	1:1	11.01	Dip-coating	150°C/2h	Hydrophilic	○
	0.1:1:0.87	0.5:0.5	11.14	Dip-coating	150°C/2h	Hydrophilic	○
	0.03:1:0.29	1:2	10.86	Dip-coating	150°C/2h	Hydrophilic	○
	0.025:1:0.22	1:3	10.83	Dip-coating	150°C/2h	Hydrophilic	○
APTMS	3.33:1:10.83	1:5	9.8	Spray	150°C/2h	Hydrophilic	○
GPTMS	4:1:26	1:0	9.8	Spray	RT/o/night	Hydrophilic	○
	2.5:1:8	1:1	7.97	Spray	RT/140°C o/night	Hydrophobic	●
	3.85:1:0.16	1:1.2	10	Spray	70°C/4h and 150°C/2h	Hydrophobic	●
TMODS	5:1:3.27	1:1.5	10.24	Spray	150°C/1h	Hydrophobic	●
TMOOS	3.78:1:5.78	1:2.6	10	Spray	RT/150°C 2h	Hydrophobic	●
		1:2.6	8	Spray	70°C/4h and 150°C/2h	Hydrophobic	●
		1:2	8	Dip-coating and spray	50°C/20h	Hydrophobic	●
		1:1				Hydrophobic	●
		2:1				Hydrophobic	●
		1:0				Hydrophobic	●
HMDS	3.78:1:5.78	1:2	6.5	Spray	50°C/20h	Hydrophobic	●
		1:1				Hydrophobic	●
		2:1				Hydrophobic	●
		1:0				Superhydrophobic	●
HMDS [49]	0.61:1:0.93	0.6:1	9			Hydrophobic	●
TMES	3.78:1:5.78	1.1:1	8	Dip-coating and spray	50°C/20h	Hydrophobic	●
TMES [61]	4:1:18.22	1.1:1				Hydrophobic	●
TMES	3.78:1:5.78	1:2	10	Dip-coating and spray	50°C/20h and RT	Superhydrophobic	●
		1:1				Hydrophobic	●
		2:1				Hydrophobic	●
		1:0				Superhydrophobic	●
		1:2	6.5	Dip-coating and spray	50°C/20h	Hydrophobic	●
		1:1				Superhydrophobic	●
		2:1				Superhydrophobic	●
		1:0				Superhydrophobic	●
		1.1:1				Superhydrophobic	●
		1:0				Superhydrophobic	●
1:0	6.5	Dip-coating and spray	50°C/24h	Superhydrophobic	●		

● Sol-gel coating modified with SiO₂ nanoparticles / ○ unmodified sol-gel coating

The measurement of the contact angles in glass, steel and PV solar panels surface reached higher contact angles when the sol-gel coatings were modified with silica nanoparticles (SNPs). These results were in accordance to literature as mentioned in the subchapter 3.1.4. - silica nanoparticles modification.

4.3. Contact angle measurements assessment

The wetting behavior of the surfaces was studied through contact angle measurements. The measurements were an average of three droplets placed in different locations of the coated surface during 1 minute each. There were very few differences between the measured water contact angles in each location which indicates the homogeneity of the surfaces. The following results summarize the best coatings achieved with TMOOS, HMDS and TMES as precursors. TMOOS precursor was not used before for this purpose and HMDS and TMES precursor were inspired in previous papers. These silanes were used to apply coatings on glass, but not on steel and on PV solar cells as done in this MSc thesis.

Firstly, a coating with TMOOS precursor was investigated, afterwards with HMDS precursor and then with TMES precursor. The best one was selected after comparing these different coatings. Its behavior was studied after application on different substrates: glass, steel and PV solar panel surface.

4.3.1. Coating with TMOOS precursor

Firstly, the contact angle measurements were made without coating application, on the three types of substrates used - Table 17.

Table 17 - Contact angles of the uncoated substrates.

Uncoated Substrates - Contact angles(°)		
Carbon Steel	Glass slides	Glass substrate from PV solar panel
57.26°	44.79°	72.63°

The wettability with TMOOS precursor was studied in both glass and steel substrates. This precursor has high potential due to its structure which is composed by a long n-alkyl chain length ($\text{CH}_3(\text{CH}_2)_6\text{CH}_2-$) which promotes strong hydrophobic interactions. According to literature, this precursor was not used before for preparing superhydrophobic coatings. The contact angles of the coating were tested by varying the molar ratios between TMOOS and TEOS precursors – Figure 25.

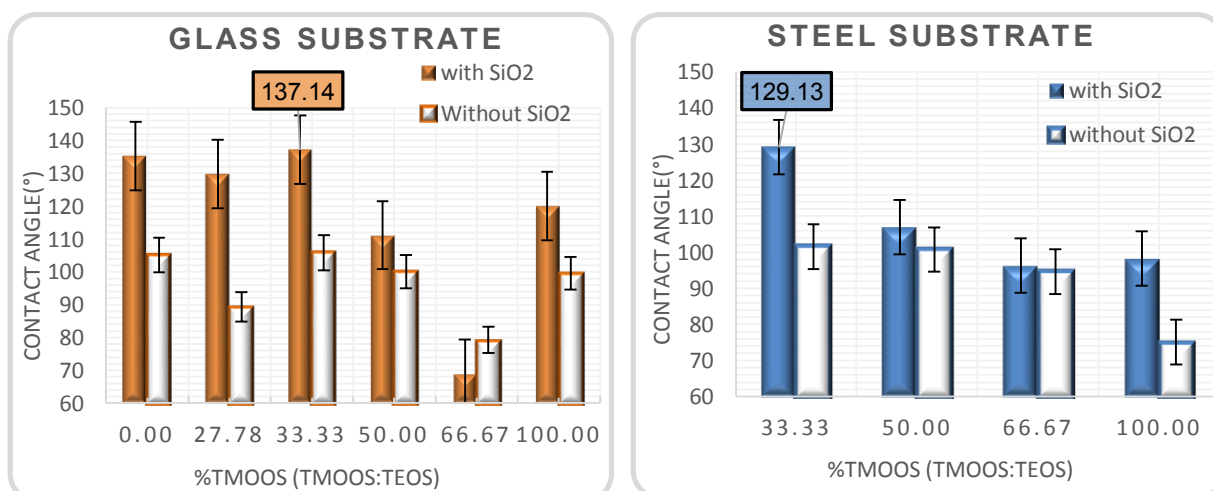


Figure 25 - Contact angles in both steel and glass substrates with different percentages (%) of TMOOS (TMOOS: TEOS molar ratios).

Table 18 presents the composition of the coatings which were used for obtaining the results depicted in Figure 25.

Table 18 - Different molar ratios used between TMOOS:TEOS.

TMOOS:TEOS	0:1	1:2.6	1:2	1:1	2:1	1:0
%TMOOS	0.00	27.78	33.33	50.00	66.67	100

The highest contact angles for both steel (129°) and glass (137°) substrates required a percentage of TMOOS - 33.33 % and addition of 1 % of silica nanoparticles to the coating. These results revealed a promising trend for future work and therefore opens the path for achieving a superhydrophobic coating with a new precursor.

The variation of molar ratios between precursors obtained non-proportional results - Figure 25 - which implies that a superhydrophobic coating can only be obtained through experimental trial. Moreover, to achieve superhydrophobicity, it is recommended to vary the pH and test different molar ratios between TMOOS and TEOS precursors.

4.3.2. Coating with HMDS precursor

This coating was inspired in the paper from Xiaoguang Li *et al.* [61]. However, only with our own formulation (3.78 mol of catalyst, 1 mol of TEOS+Si and 5.78 mol of ethanol; pH=6.5; 1 % of silica nanoparticles) the superhydrophobicity was achieved. The HMDS precursor has methyl groups which have hydrophobic properties and help promoting a higher contact angle. The highest contact angle obtained with unmodified sol-gel coating has a molar ratio between HMDS and TEOS equal to 1:2. The superhydrophobicity was achieved when was only used HMDS as precursor and with our own formulation. The best contact angle measurements achieved were 142.4° with HMDS sol-gel coating and 152.6° with HMDS sol-gel coating modified with silica nanoparticles – figure 26.

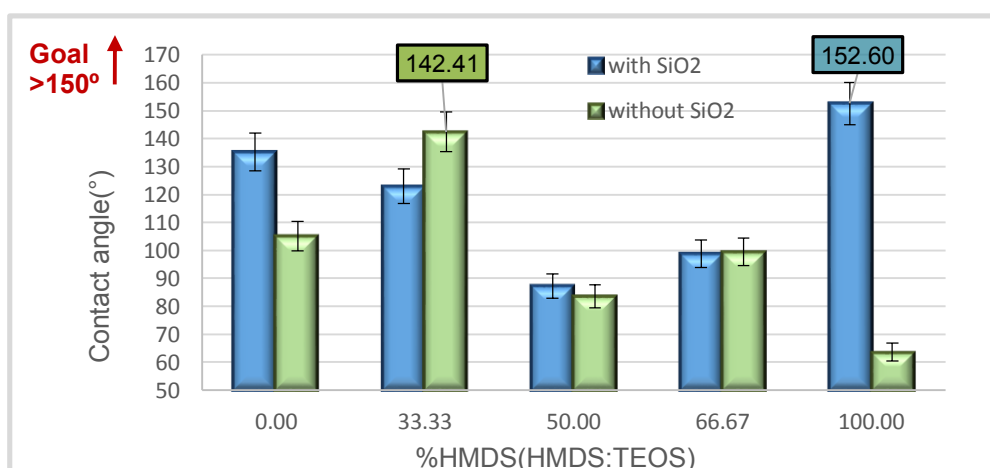


Figure 26 - Contact angle measurements on glass substrate with different HMDS:TEOS molar ratios and with HMDS sol-gel coating unmodified and modified with 1 % of silica nanoparticles.

4.3.3. Coating with TMES precursor and pH influence on contact angles

The TMES precursor was chosen due to the organic group – methyl – which promotes hydrophobicity and because was already produced superhydrophobic coatings with this silane, but was only tested in glass substrate and made with different conditions from the ones chosen in the lab experimental trial. Figure 27 evidences the dependence of the contact angles with pH. The precursor used was TMES and a comparison between Sanjay *et al.* paper [49] coating preparation and our own conditions was done. The coating made with the paper conditions did not attain superhydrophobicity. Although, with our adapted conditions the expected superhydrophobicity was achieved. Varying molar ratios between TMES and TEOS (0:1, 1:2, 1:1, 2:1 and 1:0) were prepared. For a pH equal to 10, when the molar ratios between TMES and TEOS were 1:2 and 1:0 the contact angles were 152° and 154°, respectively. Afterwards, the pH was reduced to understand the behaviour of the coating. In case the pH is equal to 6.5 the molar ratios between TMES and TEOS when were 1:1, 2:1 and 1:0 achieved contact angles between 152 and 156°. It was also tested for a TMES: TEOS molar ratio of 1.1:1 and was verified that when the TMES is increased and TEOS decreased, the contact angles increase. Another observation made was with solely using TEOS precursor which achieved higher contact angles when the pH was decreased.

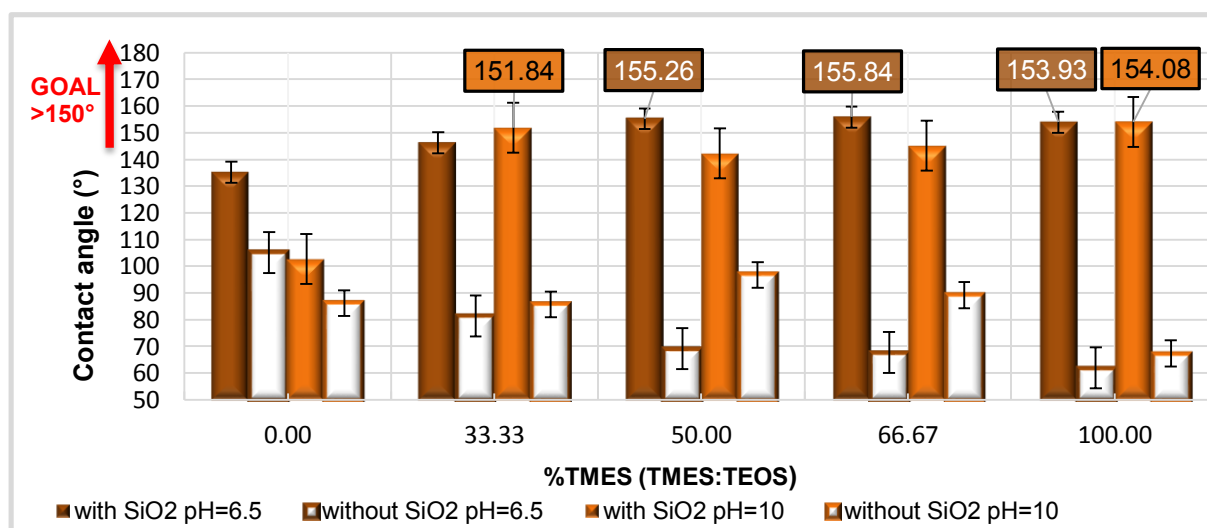
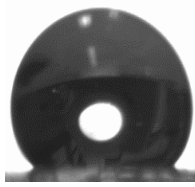
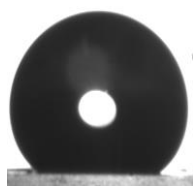
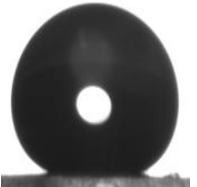
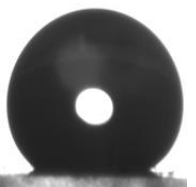
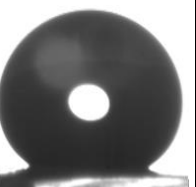
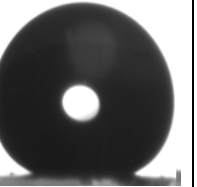


Figure 27 - pH influence on the contact angles. Variation of %TMES on the coating and application on glass substrates.

Superhydrophobicity with self-cleaning properties was maintained for a percentage of TMES equal to 100% when the pH was varied. Only static contact angles were measured through Sessile Drop method, however the coatings revealed a behaviour which seems to be the self-cleaning property. The static contact angle measurements are presented in the Table 19.

Table 19 - Contact angle measurements through Sessile Drop Method of TMES sol-gel coating modified with silica nanoparticles when the pH=6.5.

Contact angles(°)					
TMES:TEOS molar ratios					
0:1	1:2	1:1	1.1:1	2:1	1:0
					
135°	146°	155°	154°	156°	154°

4.2.4. Comparison between coatings and selection of the best one

A comparison was made between the coatings prepared with TMOOS, HMDS and TMES as precursors. The molar ratios used to compare between TMOOS/HMDS/TMES and TEOS are listed in Table 20.

Table 20 - Molar ratios applied for the three precursors attempts.

TMOOS/TMES/HMDS:TEOS	0:1	1:2	1:1	2:1	1:0
%TMOOS/TMES/HMDS	0.00	33.33	50.00	66.67	100

The hydrophobicity on glass substrate was different for each coating and the comparison was presented in the Figures 28 a) and b). Figure 28 a) and b) shows different contact angle measurements by varying the TMOOS/HMDS/TMES: TEOS molar ratios. In the Figure 28 a) the coating was modified with 1 % of silica nanoparticles and in the Figure 28 b) was used unmodified coating. The measurements were made to coated glass substrates and the conditions from the experiments were presented on Table 16. Take into account that the difference from the conditions between the preparations was the pH, which was used pH=8 with TMOOS as precursor and pH=6.5 with HMDS and TMES as precursors.

Superhydrophobicity was achieved when TMES and HMDS were used as precursors – Figure 28 a). In the case of HMDS, a superhydrophobic coating with a contact angle of 153° was obtained without TEOS addition – Figure 28 a). For the case of TMES, superhydrophobicity was achieved when the molar ratios between TMES and TEOS were 1:1, 2:1 and 1:0. The hydrophobicity was higher when the percentage of TEOS decreased and that of TMES increased. The contact angles were 146° with one third of TMES in the composition, 155° with half of TMES, 156° with two thirds of TMES and 154° with 100% of TMES.

The coating only with TMES precursor presented self-cleaning properties besides the superhydrophobicity. It was extremely difficult to measure the static contact angle because the droplets rolled-off easily when applied onto the flat surface without inclination.

In respect to the Figure 28 b) was achieved the best result with HMDS precursor. When the unmodified HMDS sol-gel coating was composed of a molar ratio between HMDS and TEOS of 1:2 it

was achieved the highest contact angle - 142°. Through Figure 28 b) it was possible to conclude that without the addition of silica nanoparticles the contact angles were lower.

Hence, the best coating has the following conditions: pH equal to 6.5, 100% of TMES precursor and the coating was modified with 1 % of silica nanoparticles. This coating was the only one which presented superhydrophobicity with self-cleaning properties and for that reason will be selected for further studies.

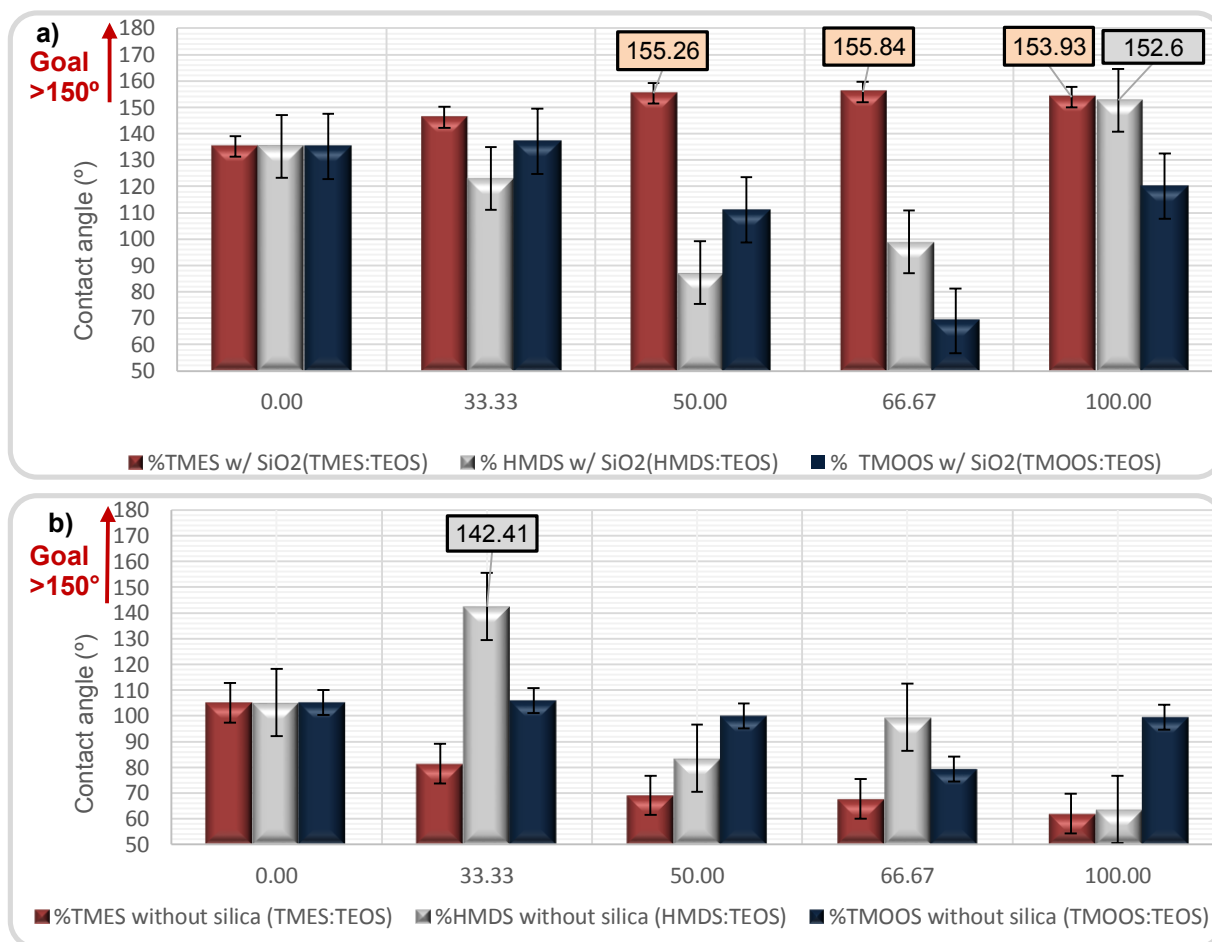


Figure 28 - Comparison of the contact angles in the glass substrate and using different silanes. (a) with the addition of SiO₂ nanoparticles and (b) without the addition of SiO₂ nanoparticles.

4.3.5. Comparison between different substrates and coating applications

This subchapter intends to present the contact angle measurements for different substrates and coating application techniques. The coating used was solely with TMES precursor and was compared the contact angle measurements with the coating unmodified and modified with silica nanoparticles.

Figure 29 shows the contact angles obtained for glass and steel substrates - Figure 29 a) were the results obtained for spray application and Figure 29 b) for dip-coating application. The superhydrophobicity was achieved for the coatings modified with silica nanoparticles. In respect to the glass substrate, the contact angles by spray coating and dip-coating application were 155° and 154°, respectively. In case of steel substrate, the contact angle for spray coating was 152° and for dip-

coating technique was 156°. In case of the coating without the addition of silica nanoparticles, the coatings presented hydrophilicity.

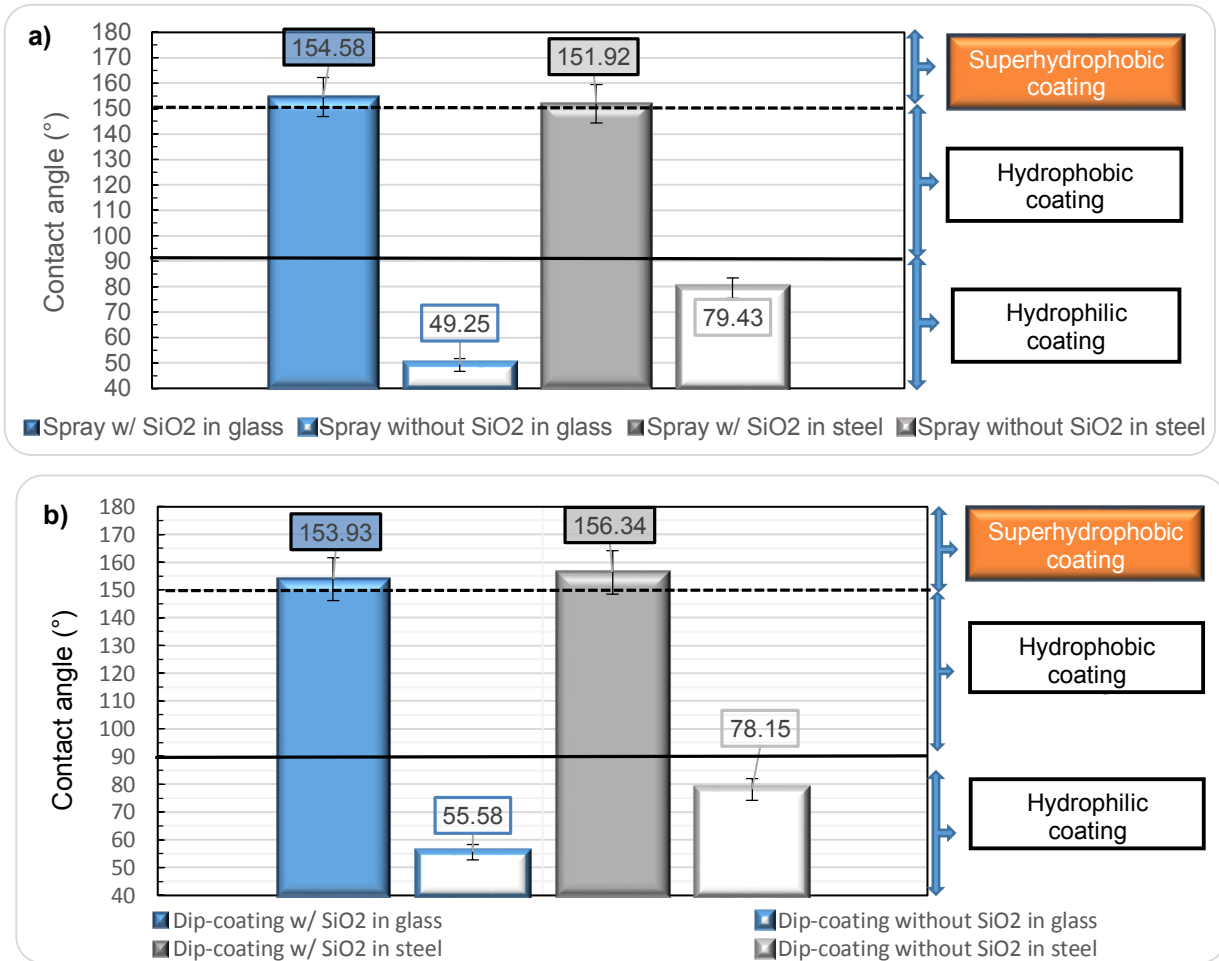


Figure 29 - Contact angles from the TMES sol-gel coating with and without SiO₂ by spray (a) and dip-coating (b) application to both glass and steel substrates.

Afterwards, the coating was applied onto the glass substrate from commercialized PV solar panels, which is composed by amorphous solar cells – Table 15 [65]. The application of the coating was made by a thicker layer of spray coating (sprayed three times), a thinner layer of spray coating (only sprayed once) and by dip-coating technique. The contact angles obtained by applying the coating onto the solar panel surface are depicted in Figure 30. TMES sol-gel coating modified with silica nanoparticles achieved superhydrophobicity with contact angles above 156° regardless the application route. When it was sprayed once and three times, the contact angle was in both cases 157° and through dip-coating application was attained the highest contact angle which was 158° - Figure 30.

The coatings were hydrophobic when the TMES sol-gel was not modified with silica nanoparticles (SNPs) and through spray coating the contact angle reached the highest contact angle, which was 120°.

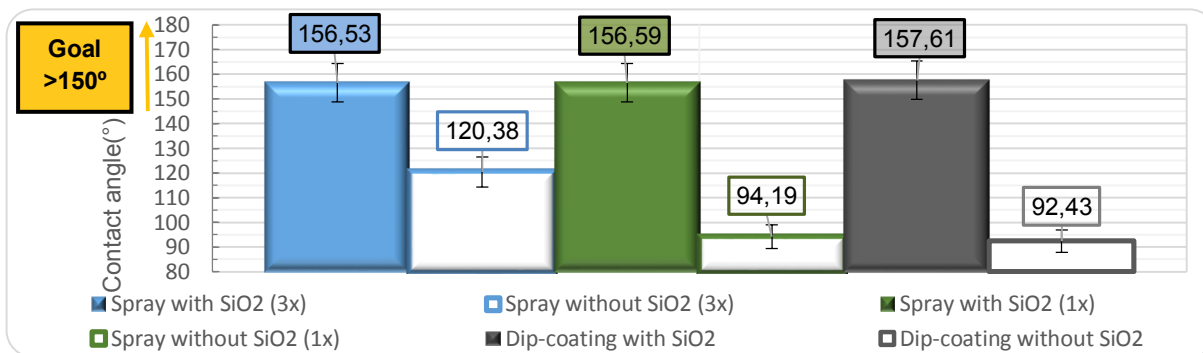
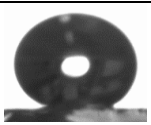
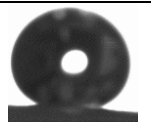
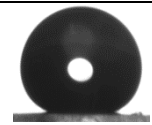


Figure 30 - Contact angles with TMES sol-gel coating without and with addition of silica nanoparticles obtained in the solar panel surface through spray coating (3x and 1x sprayed) and dip-coating techniques.

The best results obtained for the coating applied onto glass, steel and solar panel surface are presented in Table 21. Furthermore, it was concluded that TMES sol-gel coating modified with silica nanoparticles presents superhydrophobicity with self-cleaning properties, regardless the substrate and coating application route.

Table 21 - Best contact angles achieved with TMES sol-gel coating modified with silica nanoparticles in glass, steel and PV solar panel surface.

Contact angles(°)		
Substrate		
Glass	Steel	Solar panel
 155°	 156°	 158°

The self-cleaning property was observed on TMES sol-gel coating modified with silica nanoparticles. The droplet rolled-off the surface easily when the sliding angle (SA) was zero or close to zero, so it was necessary to do many attempts until a droplet fixed on the surface. A reason why it was possible to measure the contact angle was that the droplet found a particle in the surface that helped to fix the droplet for static contact angle measurements. Although, with slightest vibrations or small air dislocations, the droplet rolled-off. In case the substrate was tilted, all the droplets independently of the size, rolled-off the surface. It was not possible to use an equipment to measure the dynamic contact angle. However, it was possible to visualize that the sliding angle should be almost zero, which means that the coating may be considered self-cleaning (Figure 31). All the substrates presented the same behaviour when placed onto a flat surface. As mentioned previously, in the subchapter 3.2.1. - Contact angle measurements, the substrate was placed in the chamber of the goniometer and also in a flat bench in the lab. Afterwards, a microsyringe was used to apply droplets with different sizes and distances and in any case the droplets rolled-off fast as it can be seen through the pictures taken by the camera from the goniometer equipment – Figure 31.

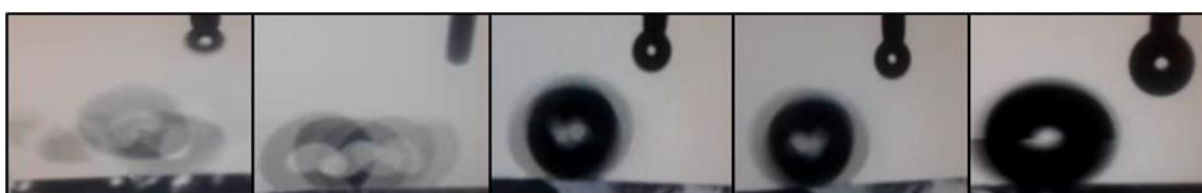


Figure 31 - Self-cleaning observation (SA<10°) through multiple shots taken by a digital camera while measuring the static contact angles in the goniometer with the different substrates.

4.3.6. Final coating conditions and results

The conditions of the coating with the best results which is going to be characterized in the following subchapters is presented on Table 22.

Table 22 - Formulation, conditions and contact angle measurements from the best coating achieved.

Si (silanes)	Molar ratios		Modified	pH	Application	Substrate	Curing	Contact Angle(°)
TMES	H ₂ O:Si+TEOS:EtOH	Si:TEOS	1 % of silica nanoparticles	6.5	Spray	Glass	50°C 20h or RT	155
	3.78:1:5.78	1:0				Steel		152
						PV solar panel		157
					Dip-coating	Glass		122
	Steel	156						
	PV solar panel	158						

The dip-coating conditions which achieved superhydrophobicity, were: three immersions of the substrate into the coating and with a withdrawal speed of 1 (4 cm/min). When the speed was 4 (16 cm/min) and the number of immersions was only one the results revealed a hydrophobic coating. Besides the final coating having the same properties independently of pH and substrate variation, the curing conditions were also compared. It was possible to notice that the final coating was independent of the curing conditions. When left for 20h at 50°C in the oven the contact angle was 156.59° and when it was left drying at room temperature (RT) the contact angle was 157.02°. This is a very important achievement since there is no need of a curing step. Regarding these results there were no differences between each condition. So, the thermal stability of the coating properties was observed. For previous coatings with different formulations the curing conditions were more extreme. Some were placed 70°C for 4h and 150°C for 2h and by increasing temperature the hydrophobicity also increased. However, the coating should be cured at lower temperature because it is for photovoltaic solar cells applications and the range of temperatures of the common photovoltaic solar panels have a maximum operation temperature of 80°C. Besides, in case the coating it is to be applied in already installed photovoltaic solar panels, has to be able to dry at any environment temperature. And for coatings applied during PV solar panels fabrication it is also beneficial because is not necessary to buy an oven. Although, in experimental tests was used most often a curing with 50°C for 20h or 24h because it promotes solvent evaporation. The coating was much more resistant to temperature differences with the formulation that used only TMES precursor.

4.4. Optical and Scanning Electron microscopy characterization

The characterization of the coating was made through optical and scanning electron microscopy. Firstly, it was examined the morphology of the coated surfaces on glass slides, then onto steel and afterwards onto the glass substrate from a photovoltaic solar panel. The glass substrate is presented on Figure 32 with TMES sol-gel coating and Figure 33 with TMES sol-gel coating which was modified with 1 % of silica nanoparticles (SNPs).

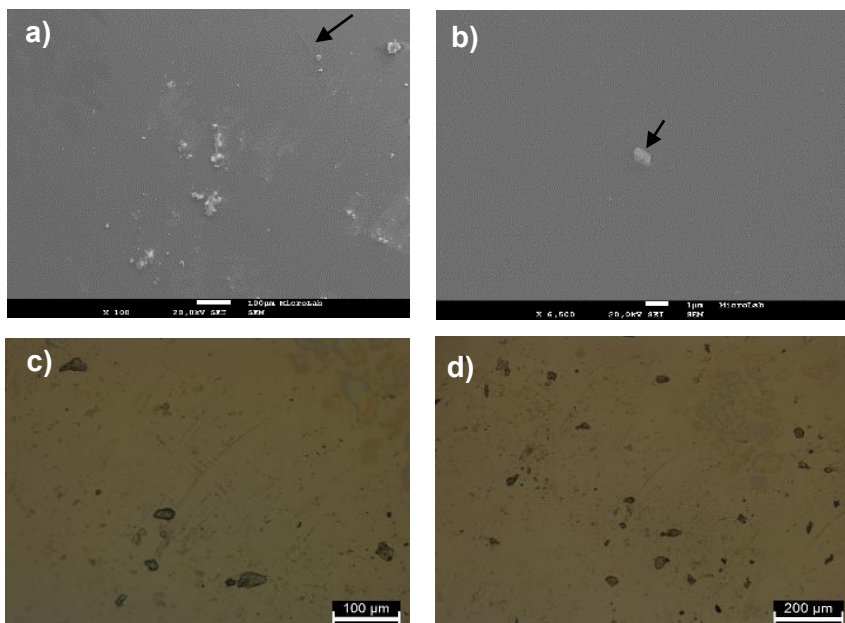


Figure 32 - Coated glass substrate (through dip-coating) with TMES sol-gel coating and HV=20 kV for SEM. a) SEM micrograph with scale=100μm and mag= 100x; b) SEM micrograph with scale=1μm and mag=4000x; c) OM picture with scale=100μm and mag=20x; d) OM picture with scale=200μm and mag=10x.

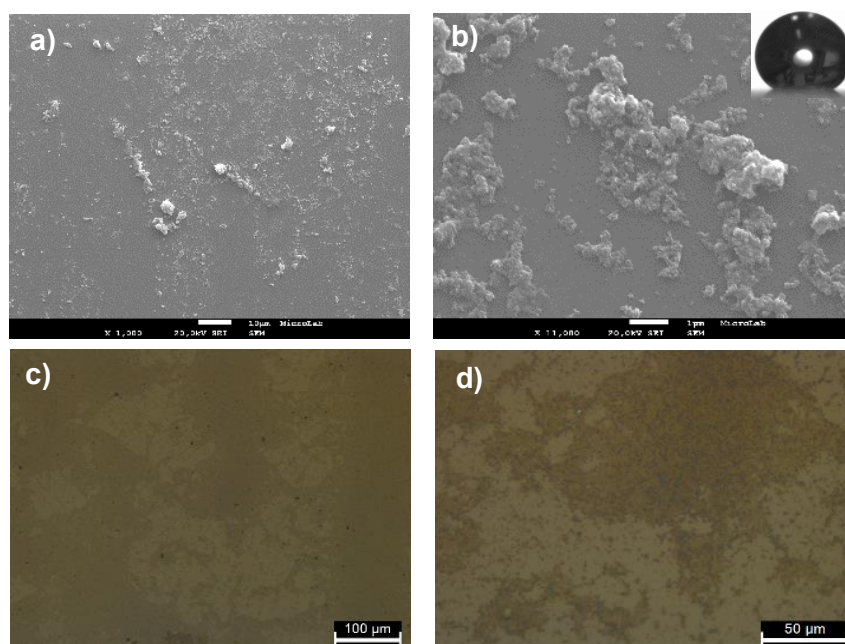


Figure 33 - Coated glass substrate (through dip-coating) with TMES sol-gel coating modified with silica nanoparticles and HV=20kV. a) SEM micrograph with scale=10 μm and mag=1000x; b) SEM micrograph with scale=1μm and mag=11,000x; c) OM picture with scale=100 μm and mag=20x; d) OM picture with scale=50 μm and mag=50x.

The glass with TMES sol-gel coating - Figure 32 a) - presented some relevant features. In the micrograph from Figure 32 b) it was possible to see a smooth surface with an average particle size of approximately $d=1 \mu\text{m}$. The irregularities may be silica related to the precursor TMES and the sol-gel process reactions - hydrolysis, polymerisation and condensation. Although, two OM pictures with the same magnification were compared - Figure 32 c) and Figure 33 c) - and the irregularities presented in the first case were different from the silica nanoparticles observed in the second which means it can be something else. The other OM pictures were also compared and the conclusion was the same. In

Figure 32 c) and d) was possible to observe a thin and transparent coating, which is beneficial for PV solar panels application. The glass coated with TMES sol-gel modified with SNPs (Figure 33) presented particles in the surface. The magnification increased from left to right and an agglomeration of particles was well defined with 11,000x. The agglomeration might be due to the cross-linking between the tetramethylethoxysilane (TMES) chain to the silica nanoparticles. Through Figure 32 and 33 it was demonstrated that dip-coating technique resulted on uniform coating distribution onto the surface. Lastly, it was possible to compare the transparency between coated glass substrate with TMES sol-gel and TMES sol-gel modified with silica nanoparticles. The surface with TMES sol-gel coating presented a perfectly transparent surface and the surface composed of TMES sol-gel coating modified with silica nanoparticles revealed agglomerates of particles. SEM micrographs presented on Figure 34 were composed by the same coating as Figure 33, but were applied through dropwise instead of dip-coating for better assessing morphological features. In Figure 34 a) it was observed an uneven surface which presented places with and without cracking. A fractured area can be visualized in Figure 34 b). However, the fractures did not affect the hydrophobicity of the coating. Through contact angle measurements it revealed superhydrophobicity ($>150^\circ$) throughout the surface. In respect to the Figure 34 c) it was possible to observe cracks at higher magnification and particles with irregular shape. The average size of three silica nanoparticles was measured and the diameter was $4.5 \mu\text{m}$. From Figure 34 a) to d) the magnification increased and in d) it was easy to visualize a thicker coating. Some advantages of using dip-coating technique were verified after analysing and comparing the micrographs of a simple drop by drop coating application. Regarding the drop-by-drop coating application, a non-uniform distribution of the coating was observed. This is a disadvantage in terms of large areas coating applications. The coating was also thick which may affect the transparency of the surface and for this reason is not suitable for PV solar cells applications. The applied coating characteristics through dip-coating has some advantages, such as to obtain thinner layers, well-distributed and cracking-free. This technique due to the several advantages presented is suitable to the PV solar panels industry application.

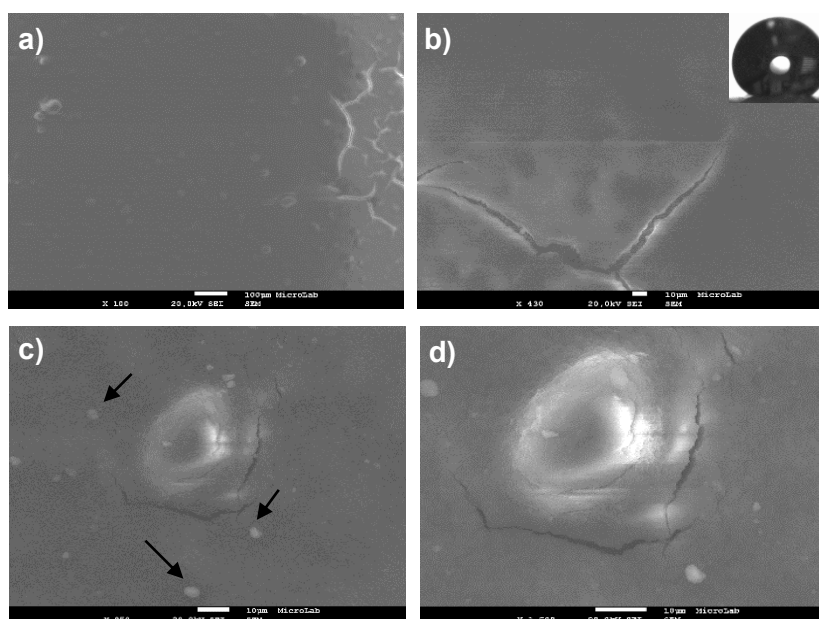


Figure 34 - SEM micrographs (HV=20 kV) of the coated glass substrate (dropwise application) with TMES sol-gel modified with silica nanoparticles: a) scale= $100 \mu\text{m}$ and mag=100x; b) scale= $10 \mu\text{m}$ and mag=430x; c) scale= $10 \mu\text{m}$ and mag=950x; d) scale= $10 \mu\text{m}$ and mag=1500x.

In case of the steel substrate, SEM micrographs with increased magnification are depicted in Figure 35 a) to d). TMES sol-gel coatings without and with modification of silica nanoparticles were presented in Figure 35 a) and b) and c) and d), respectively. In respect to the Figure 35 a), very well defined scratches in the same direction were observed and could be due to the polishing; the green arrow which was pointing to a phase contrast might be a residue. Figure 35 b) shows a smooth surface and through optical microscopy there was surface transparency. Regarding Figure 35 c) it was possible to visualize a stain on the surface, which was a darker contrast region, while the surroundings had brighter contrast. These phase contrasts can be due to the difference in silicon concentration. Darker regions represented higher amounts of silicon concentration and brighter areas a lower amount. The SEM micrograph d) with the highest magnification, showed good coverage of the surface with silica particles.

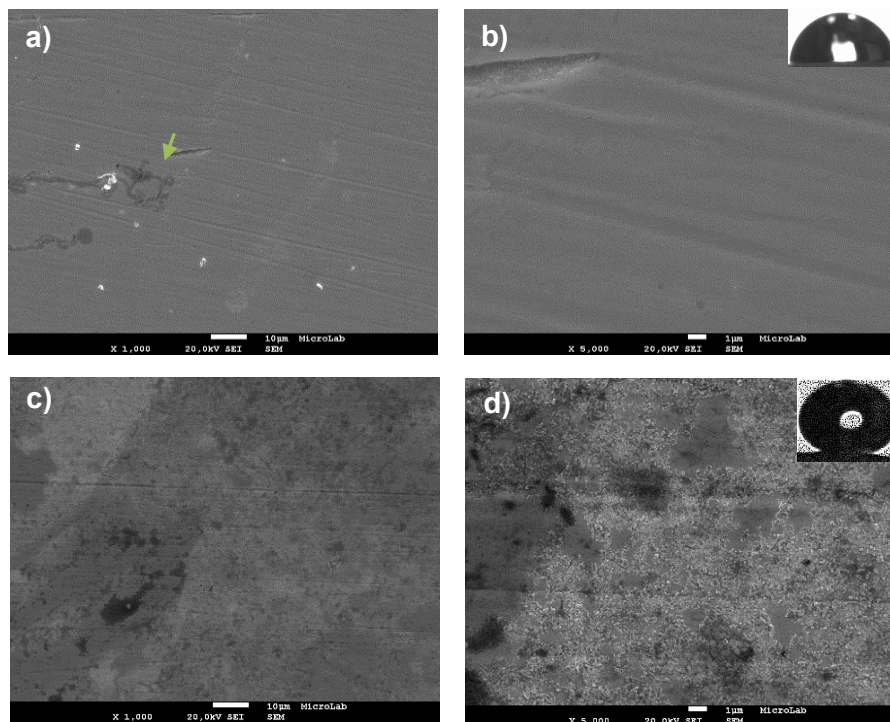


Figure 35 - SEM micrographs (HV=20 kV) of the coated steel substrate (dip-coating application) with TMES sol-gel: a) scale=10 μm and mag=1000x; b) scale=1 μm and mag=5000x. TMES sol-gel modified with silica nanoparticles: c) scale=10 μm and mag=1000x; d) scale=1 μm and mag=5000x.

The coating was also applied onto a solar panel surface. The SEM micrographs of the TMES sol-gel coating (Figure 36 a), b), c)) presented some irregularities all over the surface with a size around 6.5 μm . Through Energy Dispersive Spectrometer (EDS) it was investigated and compared the chemical composition of those irregularities and the surroundings. In the Figure 36 c) the Spectrum 1 and 2 localizations were shown and in Figure 37 the chemical composition comparison between both was made. The chemical composition of the irregularities was the same as expected from the coating proportions (Figure 37). Another important aspect is that neither cracks nor fractures were observed along the surface, so the integrity of the coating was not affected by any defect. The SEM micrographs also showed a thin coating and through OM was observed a transparent coating.

In respect to the TMES sol-gel coating modified with silica nanoparticles - Figure 36 d), e), f)) - it was possible to observe a different surface morphology. The SEM micrographs also show the round shape silica hydrophobic particles with $d < 10$ nm and agglomeration of the particles. Those agglomerations of SNPs aggregated together forming nanostructures - clusters - which may promote the superhydrophobic properties [75]. Despite the observation of a few cracks, a homogeneous and thick coating was generally observed.

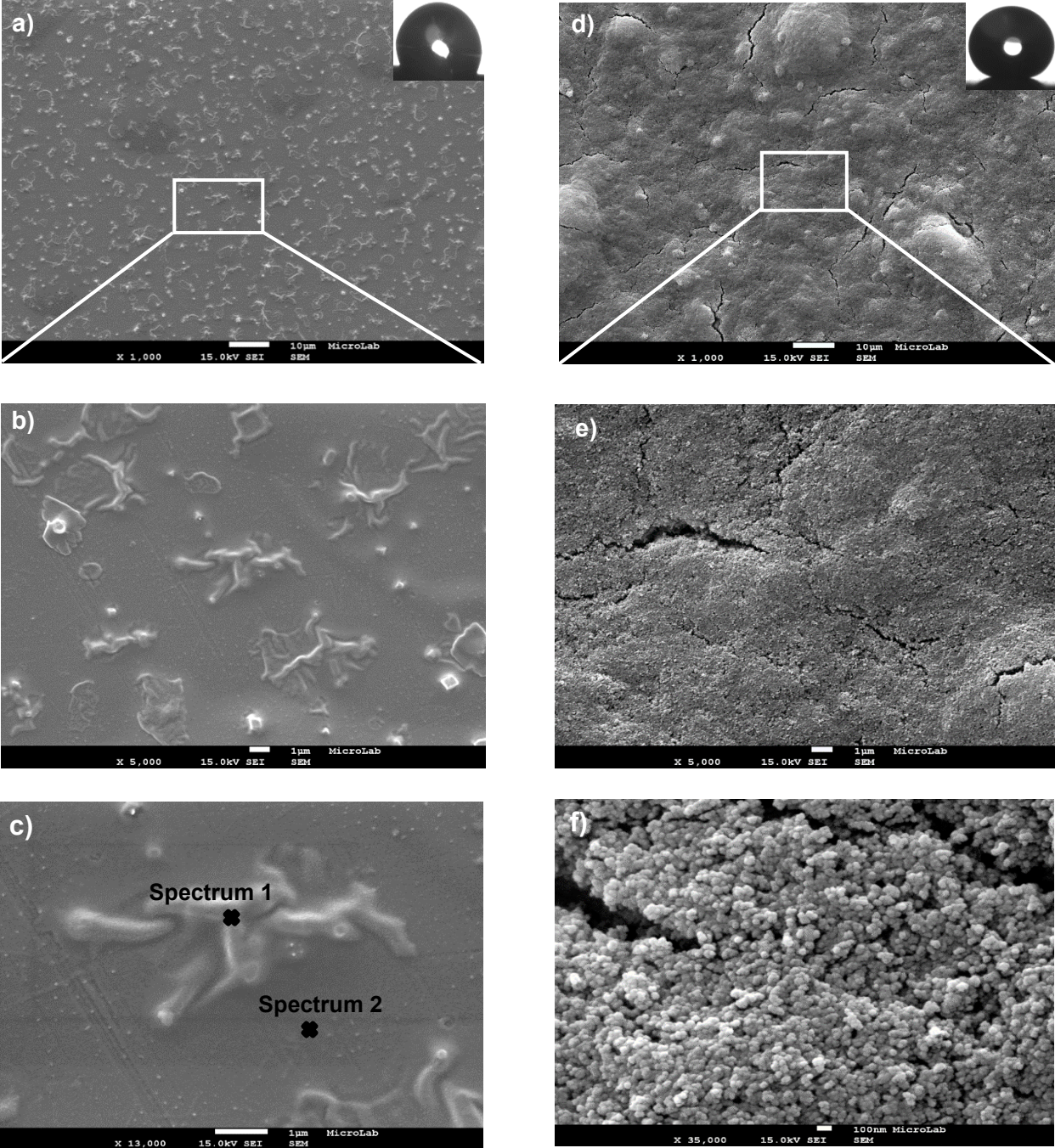


Figure 36 - Solar panel coated with a), b), c) TMES sol-gel and d), e), f) TMES sol-gel modified with silica nanoparticles. SEM micrographs with HV=15 kV: a) scale=10 μ m and mag=1000x; b) scale=1 μ m and mag=5000 μ m; c) scale=1 μ m and mag=13,000 μ m; d) scale=10 μ m and mag=1000x; e) scale=1 μ m and mag=5000 μ m; f) scale=100 nm and mag=35,000x.

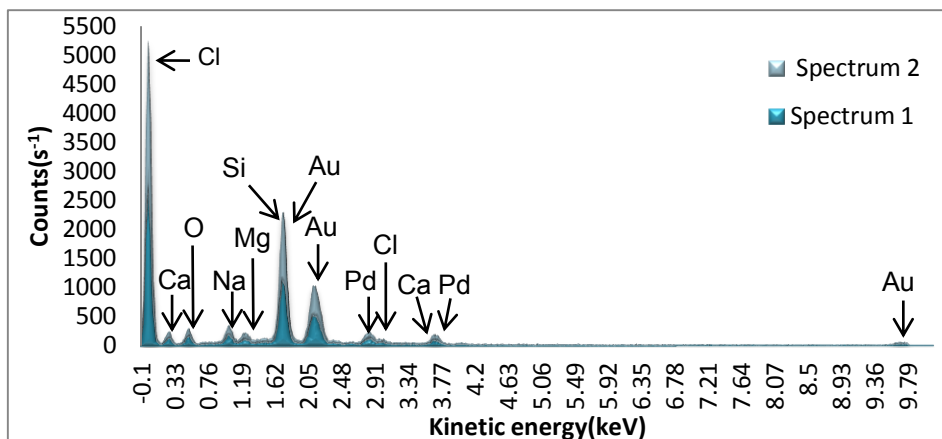


Figure 37 - Energy Dispersive Spectrum (EDS) from the PV solar panel with TMES sol-gel coating. Spectrum 1 formation and surroundings - Spectrum 2 - are shown on Figure 36 c).

4.5. Transmittance measurements

These measurements were made on glass substrates to assess the transparency of the coating. The transparency was studied when was computed the percentage of transmission (%T). Both are proportional, so when the percentage of transmission increases the transparency also increases. The transparency between TMES sol-gel coating and TMES sol-gel coating modified with silica nanoparticles was compared. The wavelengths ranged between 300 and 700 nm. Regarding Figure 38, the TMES sol-gel coating was antireflective because the percentage of transmission was 100% and TMES sol-gel coating modified with SNPs revealed an average of 91% of transmission along the wavelength interval. It was also noticed a decrease in optical transmission at lower wavelength values.

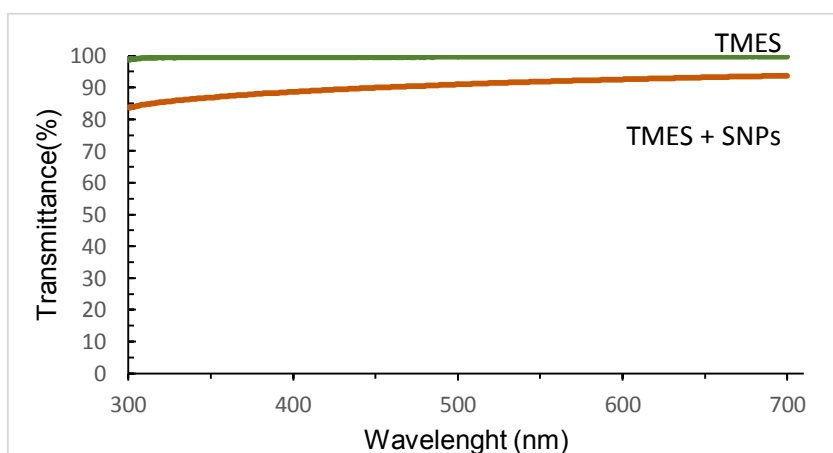


Figure 38 - Optical transmission spectra for glass samples with TMES sol-gel coating and TMES sol-gel coating modified with silica nanoparticles (SNPs).

4.6. Solar cells efficiency evaluation

Efficiency is an extremely important parameter to evaluate the influence of the coating applied on the solar cell performance. For this study were used two organic solar cells encapsulated with glass. Each solar cell revealed different efficiencies due to the active layer characteristics. Firstly, it was measured with light, the uncoated surface current in function of the applied voltage for both organic cells. Afterwards, it was done the same, but with a surface with TMES sol-gel coating in the organic cell 1 and with TMES sol-gel coating modified with SiO₂ nanoparticles (SNPs) in the organic cell 2. The data was transformed into J-V curves (Current Density (mA/cm²) – Voltage (V) curves) and the following performance parameters were evaluated to calculate the final efficiency: J_{sc} (short-circuit current density), V_{oc} (open-circuit voltage), P_{max} (maximum power point) where current density(J) and Voltage (V) achieve the maximum values, FF (fill factor) and η (efficiency). Equations (9) and (10) were used to compute the results - see 3.2.5 Solar cells efficiency evaluation. Table 23 depicts the performance parameters obtained for both organic solar cells.

Table 23 - Organic cells performance parameters: J_{sc}, V_{oc}, P_{max}, FF and η with uncoated and coated surface.

		J _{sc} (mA/cm ²)	V _{oc} (V)	P _{max} (mW)	FF (%)	η(%)	η _{uncoated} - η _{coated} (%)
Organic cell 1	Uncoated surface	-2.627	0.944	1.485	59.51	1.485	0.244
	Surface with TMES sol-gel coating	-2.419	0.975	1.241	54.00	1.241	
Organic cell 2	Uncoated surface	-7.229	0.947	3.743	54.49	3.743	0.354
	Surface with TMES sol-gel coating modified with SNPs	-6.914	0.968	3.389	51.59	3.389	

In order to compare the efficiency in uncoated with the coated surface of organic solar cells, it was necessary to plot the J-V curves for each solar cell – Figure 39. The efficiency of the organic solar cells decreased 0.244% when coated with TMES sol-gel and 0.354% when coated with TMES sol-gel modified with silica nanoparticles. These results demonstrated that TMES sol-gel coating modified with SNPs affected more the efficiency of the organic solar cell compared to TMES sol-gel coating. It is worth to notice that both coatings can be applied in PV solar cells industry because the efficiency reduction after coating application is acceptable. This decrease in efficiency of the coating is considered acceptable due to the advantages of the higher percentage of transmission (%T), superhydrophobicity (>156°) and self-cleaning properties with a flat or titled PV solar panel which surpasses this drawback.

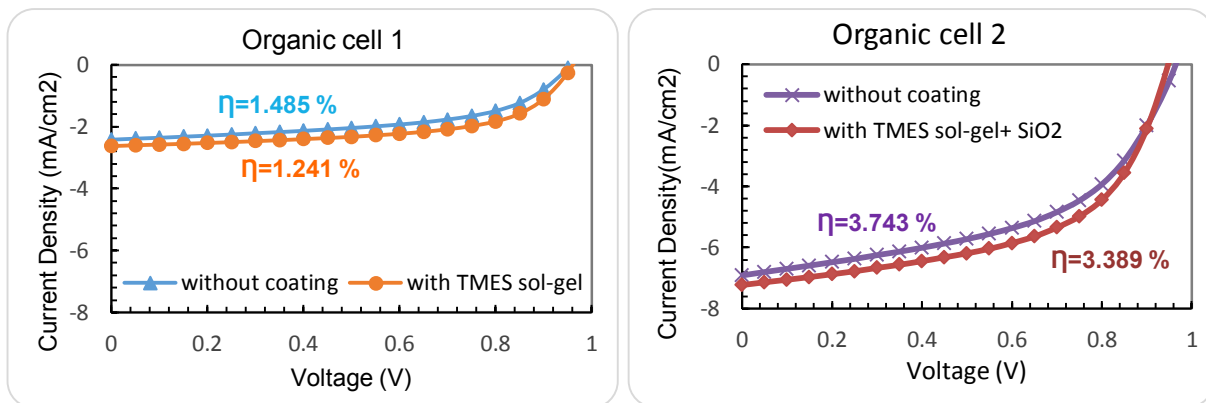


Figure 39 - J-V curves. Organic cell 1 - comparison between uncoated and coated surface with TMES sol-gel coating; Organic cell 2 - comparison between uncoated surface and surface with TMES sol-gel coating modified with silica nanoparticles.

4.7. General discussion of the experimental results

This Master Thesis provided useful insights to solving problems related to the maintenance of photovoltaic solar panels.

The renewable energies are very important, but some expenses should be reduced in order to invest in this market. Although, some progress has been made, but more has to be done. Photovoltaic solar energy had a fast development since the energy crisis. However, other problems have been forgotten despite the solar cells development and improved efficiency throughout the years. The expensive maintenance of PV solar panels is an obstacle against the development of this type of renewable energy. In order to solve this problem, this MSc thesis aims to produce a superhydrophobic coating with self-cleaning properties to apply in the maintenance of PV solar panels industry.

But what is the difference to what has been done before? The difference from this thesis is the unique coating solution which is to produce a coating compatible both with steel and glass substrates. This solution allows the application of only one coating for both materials present in photovoltaic solar panels. Glass substrate because the PV solar cells surface is constituted by glass and needs to be clean to remain with the maximum efficiency and steel which is part of the supported structure of the solar panels. The application of these coatings on solar cells has not been sufficiently explored until today. This thesis pursued and obtained a superhydrophobic coating with self-cleaning properties. This coating is expected to optimize the energy collection of PV solar panels through water and dust-free properties which maintains the surface clean. Taking into account that the coating is to be applied into PV solar panels, it is also intuitive that it should be anti-reflective and it should not reduce the efficiency substantially.

Since the beginning of the 21st century that research in superhydrophobic coatings with self-cleaning properties has increased significantly. Glass substrates are mostly used for coating application since it is used in several practical materials, such as windshields, eyeglasses, windows of high rise buildings and more recently, in solar cells. There is scarcity of information in solar cells applications. The few recent studies claim superhydrophobic coatings with self-cleaning properties applied to photovoltaics were: Hyo Jin Gwon *et al.* (2014) [3], Wang & Yung-Yeh Shu (2013) [50], Ligang Xu *et al.* (2014) [51], Gao *et al.* (2014) [76], Shing-Dan and Yan Liu *et al.* (2012) [77]. Despite being reported in the papers

that the coating can be used in solar cells, the experimental work from the literature mainly used glass as substrate. Usually, the literature work make use of glass slides and generally published work do not report compatibility with other substrates such as solar cells or materials from the structure of a PV solar panel – a unique coating solution. This unique coating solution is a R&D improvement on coating maintenance of PV solar panels. What is new, compared to the other coatings proposed before, is the possibility of using only one type of coating on different types of solar cells and steel supporting structures instead of using one for steel and another for glass substrates. Although, the development of this coating can only be made by discussing the advantages and disadvantages of this solution.

The pros from this coating are:

- ❖ An inexpensive solution – cheap in small-scale applications and can be more expensive in large-scale applications due to the large area of coating application (€/m²). Through the economic assessment which will be presented after, the coating maintenance in large-scale PV solar plants are a better option compared to other types of maintenance.
- ❖ Easy application – by spraying the PV solar panels with the coating solution or by dip-coating or spray coating during the fabrication of PV solar panels.
- ❖ Reduces the use of water – a high advantage, especially because most of the largest PV solar panels in the world are present in deserts or in remote areas and there is no access to water. It is also important to mention that at same time that fossil fuels are disappearing, also water is a precious resource which day by day is being more limited and should be avoidable to use in these cases. Besides, the water used in manual maintenance is of large amounts, so it has a big impact.
- ❖ Maintain the PV solar panel efficiency – regarding the superhydrophobic coating with self-cleaning properties, the PV solar panel remains clean and the sunlight absorption to electricity production is kept constant. Lack of rainfall, atmospheric pollution, sand dust and dusty weathers with relative humidity (RH) are some of the reasons to the PV solar panels remain unclean and self-cleaning coatings solve that problem.
- ❖ Higher energy production through the lifetime of a PV solar panel due to the reasons from the last point, which mentioned that the coating helps maintaining the efficiency of the PV solar panel.
- ❖ The energy losses with this coating are smaller than not using any coating.

And the drawbacks of the coating are:

- ❖ The spray application of the coating should be very well distributed over all the PV solar panel surface in order to avoid uneven distributions - site-specificity.
- ❖ Coating re-application has to be performed carefully in order to avoid reducing the optical performance – avoid a thick film.
- ❖ To achieve superhydrophobicity the roughness of the surface is increased and the transparency of the surface decreases. In order to achieve a superhydrophobic and anti-reflective coating, a balance has to be made to obtain a thinner film [53].
- ❖ Other obstacle is to produce a superhydrophobic, self-cleaning and anti-reflective coating which is also mechanically robust. The durability is extremely important in PV solar cells application in order to have a slower degradation and to be resistant to weather adversities [53].

The sol-gel process was used in order to prepare the intended functional coating. Through this synthesis route multiple reactions occurred (hydrolysis, condensation, polycondensation and reverse reactions) until achieve the final coating. Each step of the process was chosen carefully, since the nature of the precursor, pH region, acid or base catalyst, precursors (Si: TEOS) molar ratios variations, catalyst/precursor/solvent molar ratios and curing conditions. The precursors used were organoalkoxysilanes. During the experimental work several silanes were tested and the ones that revealed better results were: trimethylethoxysilane (TMES), trimethoxy(octyl)silane(TMOOS), hexamethyldisilazane (HMDS) and a mixture of tetraethoxysilane, TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) with the previous silanes. The precursor TMOOS was selected due to its long alkyl chain length, which promotes hydrophobicity. In case of TMES [49] and HMDS [61] precursors the state of the art revealed some work that already used these precursors to produce superhydrophobic coatings. Although, in the literature they were only tested on glass substrates.

SEM characterization was done to identify possible cracking, defects or damages on the coating surface. This characterization can also evaluate if the structure is thin or thicker, and to assess the formation of agglomerations, cross-linkages between chemical components and uniformity of the coating. Despite some differences of the coating applied onto glass, steel and solar panel surface, all of them presented good coating characteristics.

The transmittance measurements were used to study the anti-reflectance capacity of the coated substrate: the higher the transmittance percentage, the higher the transparency and better is the coating. An efficiency evaluation of the organic solar cells was also done to assess if the coating applied affects or not the efficiency of the device. The transmittance and efficiency is only slightly affected by the coating, so the novel coating can be applied onto photovoltaic solar cells industry. The results obtained in this MSc thesis has also shown that the coating has a high potential to be applied in this field because it is inexpensive, simple to fabricate and easy to apply.

5. Economic Methodology and Assessment – the use of coatings instead of manual maintenance in PV solar panels

Presently, due to the quick science evolution, it is getting more difficult to find innovative ideas to improve technologies. The product of this master thesis is a unique coating solution that intends to substitute other types of maintenance. However, a great scientific achievement idea may be not a viable result. For this reason, there is the need of an economic assessment to have a clear picture of the benefits and viability of the proposed unique coating for the maintenance of PV solar panels instead of manual maintenance. Firstly, the viability from the investor perspective and respective benefits are presented. The coating selected was the TMES sol-gel coating modified with silica nanoparticles because it revealed superhydrophobicity and promising self-cleaning properties.

5.1. Viability study from the investor perspective (energy producer)

5.1.1. Which sells energy to the distributors

In an overall point of view, the market price fluctuations determines the behaviour from the energy producer investment and also from the distributor. The distributor can choose between buying endogenous or renewable energies. Coal resources in Portugal are almost extinguished and the renewable energies gave the opportunity of producing our own alternative energy. Despite all these facts, the market price has a strong correlation with the price of endogenous energies and the final decision from the distributor will depend mostly from this factor.

If the final option is to sell renewable energies, such photovoltaic solar energy, the coating maintenance is extremely important. Solar industries demand for more efficient, less costly and durable coatings. Developing new components and materials is essential to be possible to yield higher efficiencies. From an economical point of view, such development must eventually be associated with a cost reduction [7].

5.1.2. Physical investment is done in PV solar panels already installed which implies a financial value of €/m²

In order to apply coatings maintenance, the cost is dependent on the area of each solar panel (€/m²) due to the amounts of solution required. The panels are already installed and someone must reach the location (plant operator or an outside supplier) and apply a spray coating over each photovoltaic solar panel. It is important to remind that each coating cost varies depending on the material and coating technology used. If the application of the coating is made from someone outside the installations the expenses will be higher compared to the plant operator. Also the access is costly due to the transportation costs (included in labour). Therefore, the microgeneration installations have higher labour expenses per square meter compared to PV solar plants.

Another alternative is to apply the coating to PV solar panels during production and despite the investment in machinery in the process will be cheaper due to absence of labour costs.

5.1.3. Implies a reduction in maintenance cost

After a given period of time the coating degrades and the absorbed energy decreases. For this reason, re-coating is usually carried out by the plant operator to recover the initial performance. The factors to take into account are: additional costs (material and labour) and a temporary shutdown of the receiver during the recoating process. If the number of reapplications is high, the total downtime will be also longer and the energy produced will be lower [78]. The surface of the PV solar panels remains clean when is used coating maintenance. Consequently, the transmission of light onto the solar cells increases which will increase the efficiency from the PV solar panels. In case of manual maintenance, the surface of the PV solar panels is clean when there is maintenance and then starts to accumulate dust onto the surface and decreasing efficiency. Manual maintenance requires more cleaning frequency and the time during cleaning- downtime - is higher compared to the use of coatings as maintenance.

A PV solar panel is planned for an average lifetime of 30 years. Generally, when selective coatings are used, the cleaning processes and re-coating are made at intervals of 10 years (1 initial application and more 2 reapplications in 30 years) and the reapplication downtime is around 15 days. Depending on the environment, the degradation rate of the coating can vary. A single reapplication at halfway through the plant lifetime is recommended for coatings which degrade slowly. In case of intermediate and early degradation of the coating, the optimal reapplication is estimated with an interval of 2.5 years [78].

The cost of chemical agents is not expensive and the fabrication of the coating is not difficult which means the ratio of manufacturing cost to benefit is not high. Although, the ratio of cost to benefit will further decrease in large-scale applications and for that reason developments are always being made in order to improve [7].

As mentioned before in the subchapter 2.2.2. Cleaning Frequency, the manual maintenance frequency varies from case to case. Some of the factors which influence the maintenance frequency are: type of climate and weather adversities. Manual maintenance usually is yearly which means that within 30 years lifetime of a PV power plant, a PV solar panel will have to be cleaned 29 times and will have a downtime of 145 days. So, without any coating (bare substrate) and with manual maintenance will be necessary to clean more frequently and the downtime will be much higher compared to coating application. Manual maintenance also requires a higher number of technicians to clean the solar panels, more equipment and materials. Also during the year without cleaning there is dust accumulation on the solar panels surface, which means lower amounts of sunlight will be absorbed which implies less efficiency and energy production is reduced.

5.1.4. Implies annual average efficiency increment from the panel

Superhydrophobic coatings with self-cleaning properties decrease dust accumulation in photovoltaic solar panels surface. Furthermore, the transmission losses decrease, the power losses reduce substantially, the daily energy losses become less important, which means increased daily efficiency. So, in overall the performance from a photovoltaic solar panel improves. In order to know the energy

produced by a photovoltaic solar panel in a certain location is necessary to monitor the ambient temperature and the incident solar irradiance acquired by a pyranometer (equipment used to measure solar irradiance on a planar surface). The incident solar irradiance is obtained through measurements and estimations over a horizontal or fixed tilt plan. A higher energy absorption is obtained with tilted planes. Other aspect which influences the global irradiance is the time of the year. In Portugal, the inclination angles which maximize the absorption of solar energy should be between 50° and 60° during winter and between 5° and 10° during summer [27, 38].

Firstly, it was shown a scenario from the incident solar irradiance per square meter (kWh/m²) in a PV solar panel with different titled angles of 30° and 60°. It was intended to study the PV solar panel which observes higher monthly global irradiation – figure 40 – and in annual terms was possible to observe that with 30° was collected more energy. For further studies was chosen a tilted angle of 30° due to optimized conditions. The inclination angle chosen was in accordance to literature because the angle which maximizes the energy absorption should be close to the latitude from the location. Lisbon is 38° 43' and the average optimal angle for Portugal is 33° [17].

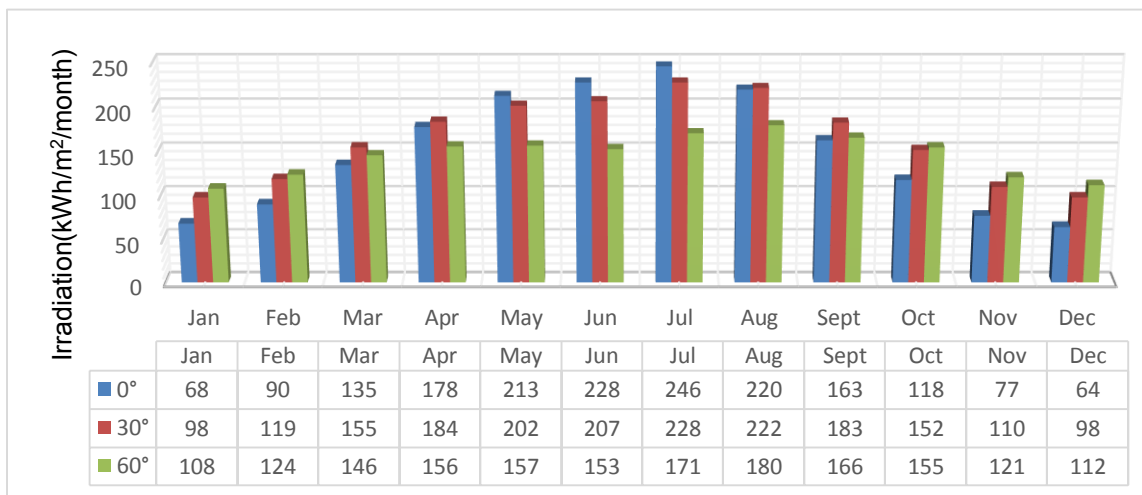


Figure 40 - Average monthly global irradiation over the horizontal and the fixed plan with 30° and 60°, in Lisbon (Adapted from [17]).

Secondly, in Figure 41 a) was presented a scenario with Portugal climate and a titled angle of 30°. In this case was assumed no losses (blue column), other assuming 10% of soiling losses between May and September (less rainfall) and 7% the rest of the year (without the use of coating) [39, 79] (red column). Other case presented was 2% of energy lost with the use of coating [39, 79] (green column). The incident annual irradiation was 1958 kWh/m²/year without any losses, 1919 kWh/m²/year with coating and 1790 kWh/m²/year without coating and losses. The energy lost with coating was 39 kWh/m²/year and without coating was 168 kWh/m²/year.

Thirdly, a scenario was made in Figure 41 b) to simulate the impacts in an extreme situation, such as deserts and the percentage of soiling losses was higher than 15% [39]. If in this situation the PV solar panel soiling losses were of 20% it will be lost 392 kWh/m²/year without the use of any coating. As

demonstrated, superhydrophobic coatings with self-cleaning properties reduce the losses in percentage of incident irradiance [37, 39].

Throughout a year the energy lost per square meter (m²) without using coating is significant. The losses in energy production without using coatings has a huge impact in case of a solar plant which has hundreds of solar panels. Other important point is definitely the location of the PV solar panels installations because high annual irradiances influences the level of productivity.

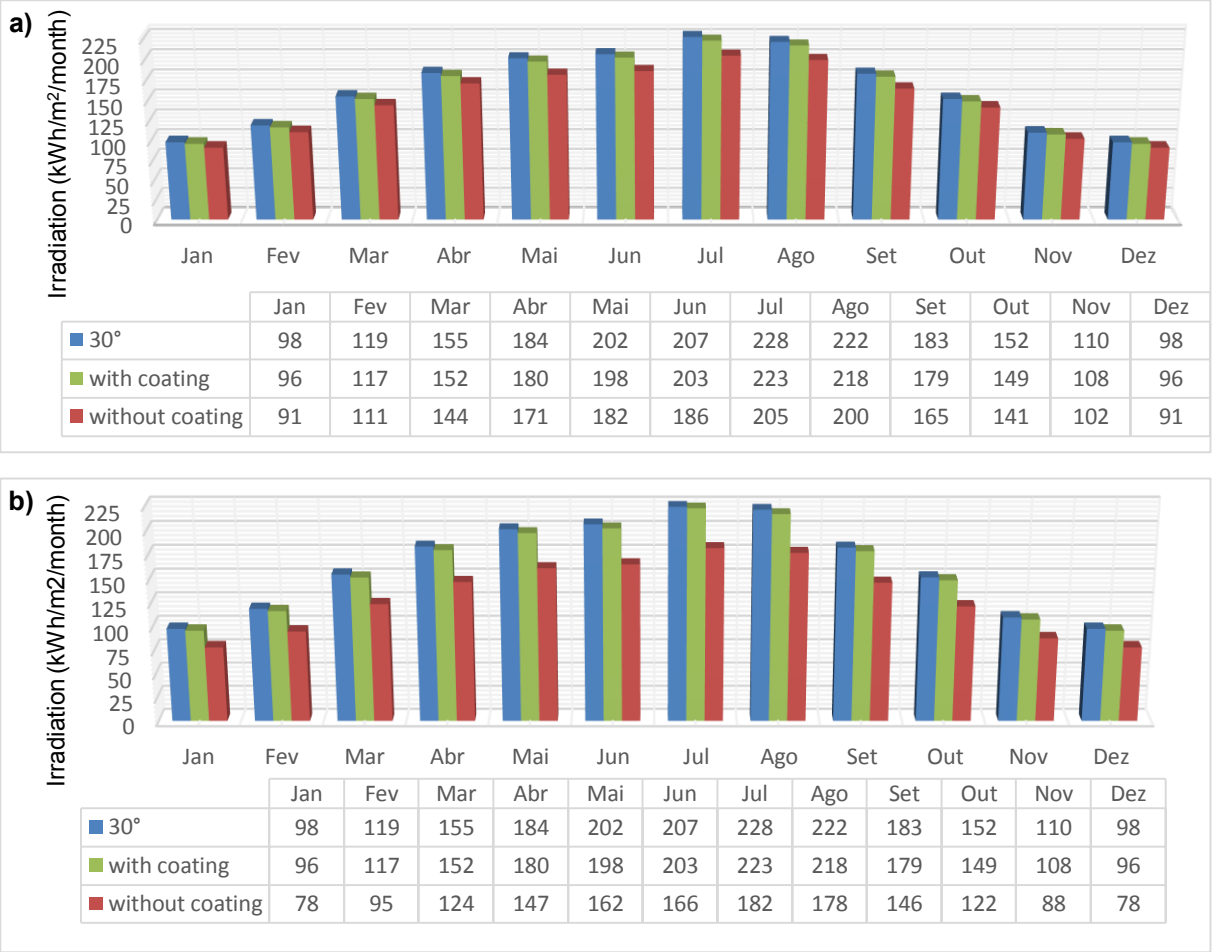


Figure 41 Average monthly global irradiation with and without coating in a titled fix plan with 30° in Lisbon (Adapted from [17]): a) with Portugal climate; b) if Portugal had an arid climate.

To perform an economic viability study, it is important to know the profitability to the investor. The investment could be made to a PV solar panel and a coating or only to the coating. In terms of computations and data available was easy to make computations applied to an already existent installation and compute solely the investment of the coating maintenance. There are two plausible approaches: to apply in an industrial installation which sells energy or is for own private consumption and the other approach is a domestic installation which is for private consumption. In the second case, the specifications from the installation are not available so the case study was made to PV solar plants already installed.

5.2. Case Study of Martifer Solar Algarve Projects

This sub-chapter introduces a Case Study which has the purpose to evaluate the possibility to implement coating maintenance to an already installed PV solar plants. The economic evaluation was made to a Martifer Solar Company Project. The PV solar plants from Martifer Solar intend to sell the energy to supply houses from outside consumers.

5.2.1. Characteristics of the PV solar plant

The Algarve Projects from Martifer Solar include Avalades PV plant and Ferreiras PV plant (figure 42). Some of the main specifications, such as the energy produced are given with the two PV plants together and for that reason the case study will be made to both PV plants together [80].



Figure 42 Avalades, Silves PV plant (left) and Ferreiras, Albufeira PV plant (right) [80].

This case study has the purpose to show the high maintenance costs savings and the higher energy produced of using coatings instead of manual maintenance. These are PV plants with extremely high dimensions which means the costs will increase. The PV plant characteristics are in the following Table 24 [80]:

Table 24 - Specifications from the PV solar plants used in the Martifer Solar case study [80, 81].

Case Study Algarve PV plants(Martifer Solar)	Avalades	Ferreiras
Capacity(MW)	15.6	6.8
System size(MW)	22.4	
Investment(Annual Report 2012)(M€) [81]	14,8	5,6
Investment Cost(Avalades+Ferreira)(M€)	20,4	
Lifetime(years)	25	
Energy Produced(GWh/year)	37.4	
Total area(m ²)	570,000	
Area from 1 module(m ²)	2	
Module Quantity(HSL 72S Poly module from Hanwa Solar)	94,400	
Area from the total modules(m ²)	188,800	

Some of the specifications from Table 24 will be used as tool for the computation of other parameters. The only investment made is the coating and for that reason the data from the PV plant investment will be used to compute de operation and maintenance (O&M) costs.

5.2.2. Coating Characteristics

Through this MSc thesis, several attempts were made in the lab to obtain the wished coating. The components for the best one are: TMES (trimethylethoxysilane), EtOH (ethanol), a pre-prepared solution of NH₄OH 2M and 1 % of silica nanoparticles, as follows (Table 25):

Table 25 - Coating constitution (small-scale).

Laboratorial Scale dimensions (for 0.06 m ² application)		
Reagents	Volume(mL)	Price(€)
EtOH	6.85	0.43
TMES	3.22	6.08
NH ₄ OH 2M	1.37	0.39
Silica hydrophobic nanoparticles (g)	0.098	0.02
Total	11.5	6.92

In order to introduce the coating into all the modules (188,800 m²) are needed 37,156 L from the solution presented in table 25. The total cost of that amount is 190,2 k€. The reagents with high purity grades were purchased from Sigma-Aldrich. Labour costs are included in the total coating price because for industrial applications the purity grade of the reagents is lower and the price of the coating will decrease substantially. Regarding this condition, only the coating expenses are counted and labour is included in this reagents prices difference. Besides the solution, the equipment and materials used are common in R&D labs.

5.2.3. Saving Costs in O&M

Martifer Solar follows another scenario called corrective maintenance and that type of maintenance suffer a large fluctuation in the costs. The PV solar plant has a lifetime of 25 years and the Operation and Maintenance (O&M) costs were divided in five scenarios and compared between manual and coating maintenance. Three sources mentioned that costs of manual maintenance are estimated to be 2% of the investment cost(IC) per year and include the charges for the replacement of the inverter in the 10th to 12th year and an insurance policy against theft and adverse atmospheric conditions which might damage the installation [27, 32, 79]. The 1st scenario was the case which often happens when the regular manual maintenance is not accomplished and is done each three years. This scenario has a cost each three years of 408 k€ and the total cost along the 25 years of 3,26 M€. The manual maintenance recommended in Portugal is yearly as represented in the 2nd scenario. In this case, the total costs after 25 years are 9,79 M€.

For Coating Maintenance, the labour from the plant operator or from an outside company, has the function to spray the panels and this was included in the materials price. As mentioned previously, the costs of the reagents for industrial applications are lower compared to the ones used in the lab, due to the purity difference from the reagents. Therefore, the labour expenses are included in the material costs. In case of coating maintenance there were three possible scenarios: a 3rd scenario with a very slow degradation coating (reapplication only halfway through PV solar panel lifetime), a 4th scenario with a coating with slow degradation coating or durable coating (reapplication every ten years, so 2 reapplications) and the 5th scenario which was the worst case scenario with an intermediate degradation of the coating (reapplication each four years). When a coating maintenance is done are payed 190,2 k€. The 3rd scenario has a total cost of 570 k€, the 4th scenario of 380 k€ and the 5th scenario of 1,33 M€. Therefore, the O&M costs for Martifer Solar (Avalades + Ferreiras) PV plant vary depending on the schedule of each one and the computation methodology applied. Coating maintenance was the best option in all the scenarios in comparison to manual maintenance.

The cost savings of using coating maintenance instead of manual maintenance achieved in all scenarios better results and with million euros of savings. The economic saves after comparing the different scenarios between manual and coating maintenance are presented in Table 26:

Table 26 - Money saved by comparing each scenario.

Comparisons	Money savings(M€)
Between 1 st scenario and 3 rd scenario	2.69
Between 1 st scenario and 4 th scenario	2.88
Between 1 st scenario and 5 th scenario	1.93
Between 2 nd scenario and 3 rd scenario	9.22
Between 2 nd scenario and 4 th scenario	9.41
Between 2 nd scenario and 5 th scenario	8.46

In extreme cases coating maintenance remains a cheaper option compared to manual maintenance. Almost 2 M€ are saved with coating maintenance when manual maintenance is done each three years and the coating maintenance is done each four years. Coating maintenance can reach saves of 9 M€ if is done a yearly manual maintenance.

5.2.4. Increments in Energy Production

The five scenarios from O&M were used to study the Energy Production profit (€/m²). Regular maintenance keeps the surface from PV solar panels more exposed to sunlight, so efficiency will be higher and consequently energy production increases. The considerations made to compute were: the decrease in energy production each year with and without coating is 2% and 10% respectively [36, 37, 38] and secondly the profit obtained from each kWh produced (Table 27) taking into account the Portuguese Decree Law – DL35 from February 28th of 2013 – is 0.036 €/kWh [82].

Table 27 - Energy production profit during the lifetime from the PV solar plant [80, 82].

Energy Production Profit (M€/ 25 years)		
Manual Maintenance	1 st scenario	27.59
	2 nd scenario	30.29
Coating Maintenance	3 rd scenario	30.57
	4 th scenario	30.40
	5 th scenario	32.02

Afterwards, was investigated the increase in energy production profit when is used coating maintenance instead of manual maintenance – Table 28. According to the results, the coating maintenance achieves always higher energy production. The difference between each type of maintenance is reduced when the manual maintenance is executed more frequently. In this case, the costs in manual maintenance increase and coating maintenance turns out to be a more cost-effective solution.

Table 28 - Energy profit gained with coating maintenance instead of manual maintenance.

Energy Profit gained with coating maintenance(M€/25 years)					
Between 3 rd and 1 st scenario	Between 4 th and 1 st scenario	Between 5 th and 1 st scenario	Between 3 rd and 2 nd scenario	Between 4 th and 2 nd scenario	Between 5 th and 2 nd scenario
2.98	2.81	4.43	0.27	0.11	1.73

5.2.5. Final Remarks

In summary, the coating maintenance applied to this PV solar plant reduces the O&M costs from almost 2 M€ to more than 9 M€ depending on the comparison between cleaning frequency scenarios. The energy profit gained was compared between coating and manual maintenance. Coating maintenance presented a huge increase in energy profit. Although, it is important to mentioned that the energy profit gained is lower when the manual maintenance frequency increases, but the expenses of doing manual maintenance more frequently are higher. Energy profit is gained with coating maintenance in any case scenario. Regarding these conclusions, this unique coating solution is profitable in large-scale PV plants applications.

The cleaning frequency recommendations were presented on sub-chapter 2.2.2. Cleaning Frequency, but in some cases the recommendations are not followed. Cleaning frequency should be decided by the plant maintenance manager considering the cleaning modules frequency according to the cost of this task and the economic value of dirt-induced losses.

In case of a small generation, off-grid installations, roof-top installations and building integrated photovoltaics (BIPV) the expenses in O&M costs are lower compared to large-scale PV solar plants. Although, the amount of energy produced is smaller in small generation, so a case study was presented.

Several studies can be made because a balance between energy production and maintenance expenses must be done. The economic evaluation not only depends on the amount of coating needed per square meter (€/m²) but also on the labour costs. The labour cost per square meter is cheaper in large-scale PV solar plants compared to microgeneration.

6. Conclusions

This MSc thesis has achieved the goal of obtaining a unique functional coating to be applied on photovoltaic solar cells. What is new compared to other coatings reported before? The possibility of using only one functional coating for glass and steel substrates which is an important tool to reduce the operation and maintenance costs of PV solar panels.

To reach the purpose were needed to be produced several coatings through sol-gel route. First, the chemical composition has to be changed until achieve hydrophobicity. The sol-gel coating was produced with different silanes as precursors. The contact angles were measured through Sessile Drop Method for the different coatings applied on glass, steel and on a PV solar panel.

Superhydrophobicity was reached when silica nanoparticles were also added to the sol-gel coating to increase the hydrophobicity. The accurate selection of reagents and experimental parameters was done by choosing the right pH, catalyst, solvent and molar ratio composition between the silane and TEOS (0:1, 1:2, 1:1, 2:1 and 1:0) precursors. TMOOS precursor, presented the highest contact angle of 137° with a molar ratio between TMOOS and TEOS of 1:2. When the same coating was applied on steel the highest contact angle was observed which reflects identical coating properties when different substrates were used. This opens a window for further research with TMOOS precursor since has never been used before for this purpose. Afterwards, several superhydrophobic coatings were obtained, such as: solely with HMDS precursor with contact angles of 153° and with multiple molar ratios between TMES and TEOS.

The pH was varied, being used 10 and 6.5 to study its effect on the coating hydrophobicity. The pH equal to 6.5 was chosen because a higher number of superhydrophobic coatings was obtained. Superhydrophobicity with pH equal to 6.5 was achieved for coatings with molar ratios between TMES and TEOS of 1:0, 1:1 and 2:1 and the contact angle values were between 154° and 156°. For further studies was selected a coating that also presented possible self-cleaning properties. The functional properties were maintained for pH equal to 6.5 and 10. This coating has the following conditions: ammonium hydroxide (NH₄OH 2M) as basic catalyst, ethanol as solvent, 1 % of silica nanoparticles and only TMES as precursor. The formulation used in the composition was: H₂O: TMES: solvent ≡ 3.78:1:5.78 molar ratio.

Regarding the coating application routes, spray coating is recommended in case of PV solar panels already installed and in industry production of PV solar panels both dip-coating or spray coating can be used. Coated glass and steel surfaces presented contact angles above 152° and coated PV solar panel surfaces achieved contact angles above 157° independently of the coating application route. Therefore, the coating compatibility with glass, steel and glass from PV solar panel surface was verified.

Optical and Scanning Electron Microscopy characterization was performed after coating application on glass slides, steel and glass substrate from a PV solar panel. The TMES sol-gel coating applied onto these substrates presented characteristics that are beneficial for photovoltaic solar panel applications, which were: a uniform distribution, cracking-free, thin and transparent coating. The coating modified

with silica nanoparticles was less transparent and presented agglomeration of particles which promote hydrophobicity.

TMES sol-gel coating also revealed optical properties when studied through a UV-Vis Spectrometer. An anti-reflective coating was obtained with TMES sol-gel coating because the optical transmission has an average of 100% which implies that the coating does not affect the light absorption and transparency of the solar cells. In case of TMES sol-gel coating modified with silica nanoparticles, the optical transmission diminished to 91%

The efficiency assessment of coated organic photovoltaic solar cells was also tested for TMES sol-gel coating and TMES sol-gel coating modified with silica nanoparticles. A slightly decrease in efficiency was obtained, but is considered acceptable if the advantages of the higher percentage of transmission (% T), superhydrophobicity ($>156^\circ$) and self-cleaning properties with a flat or tilted solar panel surpass this drawback. Besides, the novel coating is in accordance to the expectations due to the promising facile preparation, low cost and easy application on different substrates. However, despite the low percentage of addition of silica nanoparticles to the coating, the contact angles increase substantially and the transparency of the coated substrate and the efficiency of the organic solar cells decrease. So, a balance between the amount of particles which must be added to the coating should be done in order not to affect the coating effectiveness.

A comparative evaluation of the economic impact of the energy losses due to soiling in photovoltaic modules has shown that is better to use a superhydrophobic coating with self-cleaning properties on the PV solar panels surface instead of other types of maintenance. Photovoltaic power plants (Martifer Solar Algarve Projects with 22.4 MW capacity) were used as case study to know the cost saves and energy production profit of using coating maintenance instead of manual maintenance.

The cost saves and energy production profit of using coating maintenance were computed by comparing different cleaning frequency scenarios between coating and manual maintenance. The cost saves were between approximately 3 M€ and around 8 M€ and the energy profit gained ranges between 110 k€ and more than 4M€, so in all cases money is saved and the energy profit increases. Therefore, the proposed coating is a cost-effective solution as coating maintenance for large-scale PV solar plants.

7. Outlook and Future perspectives

The purpose of this Master Thesis was achieved. A unique coating, both compatible with glass and steel substrates, superhydrophobic and with self-cleaning properties was obtained.

The results provided answers but also opened many questions and thus suggestions of future experimental work. Taking into account the application of the coating into the photovoltaic solar panels, these are possible future activities:

- ↪ Verify the long-term storability to inform the client and the producer about the best conditions to store the sol-gel formulation, such as temperature conditions and local of storage.
- ↪ Evaluate the coating resistance to degradation with time. This gives the possibility to better estimate the frequency of maintenance. The tests can be performed on coated PV solar panel located outside and subjected to weather ageing and to monitor the properties of the coating for a long period of time. On the other hand, it is also possible to perform accelerated tests to check the durability of the coating. For this study Electrochemical Impedance Spectroscopy (EIS) can be used to study the behaviour of the coating in conditions simulating aggressive environments where some of the PV solar plants are located.
- ↪ To test the adhesion of the coating to the substrate with standardized tests, such as the scratch test.
- ↪ Measure the dynamic contact angles (receding and advancing contact angles) to allow the naked eye observation of the self-cleaning effect to be more consistent. Through the difference of the advancing and receding contact angles is obtained the contact angle hysteresis which must be lower than 10° to have the self-cleaning property. The equipment is not available in IST, although the equipment is named e.g. Attension Theta Optical Tensiometer.
- ↪ Improve coatings based on TMOOS precursor. This MSc thesis showed the compatibility of this coating both with steel and glass substrates for a molar ratio between TMOOS and TEOS of 1:2. Besides, the contact angle measurements revealed high hydrophobicity. This precursor was not used before to prepare superhydrophobic coatings with self-cleaning properties. In the future, it is recommended to study the effect of pH and other molar ratios between TMOOS and TEOS precursors.

References

- [1] Sayyah, A., *et al.* (2014). "Energy yield loss caused by dust deposition on photovoltaic panels." *Solar Energy*, Elsevier Journal, 107: 576-604.
- [2] He, G., *et al.* (2011). "Review of Self-Cleaning Method for Solar Cell Array." *Procedia Engineering* 16: 640-645.
- [3] Gwon, H., *et al.* (2014). "Superhydrophobic and antireflective nanoglass-coated glass for high performance solar cells." *Nano Research* 7(5): 670-678.
- [4] Park, Y.-B., *et al.* (2011). "Self-cleaning effect of highly water-repellent microshell structures for solar cell applications." *J. Mater. Chem.* 21(3): 633-636.
- [5] Ganesh, V. A., *et al.* (2011), "A review on self-cleaning coatings." *Journal of Materials Chemistry* 21(41): 16304-16322.
- [6] Lin, J., *et al.* (2013). "Highly transparent and thermally stable superhydrophobic coatings from the deposition of silica aerogels." *Applied Surface Science* 273: 776-786.
- [7] Mohamed, A. M. A., *et al.* (2015). "Corrosion behavior of superhydrophobic surfaces: A review." *Arabian Journal of Chemistry* 8(6): 749-765.
- [8] Zhang, Y.-L., *et al.* (2012). "Recent developments in superhydrophobic surfaces with unique structural and functional properties." *Soft Matter* 8(44): 11217-11231.
- [9] Gonçalves, G., *et al.* (2008). "Superhydrophobic cellulose nanocomposites." *J Colloid Interface Science* 324(1–2): 42-46.
- [10] Kumar, D., *et al.* (2015). "Development of durable self-cleaning coatings using organic–inorganic hybrid sol–gel method." *Applied Surface Science* 344: 205-212.
- [11] Deng, Z.-Y., *et al.* (2014). "Versatile superhydrophobic and photocatalytic films generated from TiO₂-SiO₂@PDMS and their applications on fabrics." *Journal of Materials Chemistry A* 2(12): 4178-4184.
- [12] Luque, A., and Hegedus, S. (2011), "Handbook of Photovoltaic Science and Engineering", Second Edition, John Wiley & Sons.
- [13] Dgs, D. (2010), "German Solar Energy Society DGS, Planning and Installing Solar Thermal Systems, A Guide for Installers, Architects and Engineers", Second Edition.
- [14] Kleidon, A., *et al.* (2016), "Physical Limits of Solar Energy Conversion in the Earth System.", *Solar Energy for fuels Journal*, Topics in Current Chemistry, Springer, 371: 1-22.
- [15] Chen, G., *et al.* (2013). "Nanochemistry and nanomaterials for photovoltaics.", *The Royal Chemistry Society Review* 42(21): 8304-8338.
- [16] Catchpole, K. R. (2006). "Nanostructures in photovoltaics." *Philosophical Transactions A of The Royal Society*, 364(1849): 3493-3503.
- [17] Castro, R. (2011), "Uma Introdução às Energias Renováveis - Eólica, Fotovoltaica e Mini-hídrica", Instituto Superior Técnico.
- [18] Corkish, R. (2013), "Solar Cells, Reference Module in Earth Systems and Environmental Sciences", Elsevier, adapted from Green, M.A. and Ho, J..
- [19] Razykov, T. M., *et al.* (2011), "Solar photovoltaic electricity: Current status and future prospects." *Journal of Solar Energy*, Elsevier, 85(8): 1580-1608.
- [20] Raval, N. and A. K. Gupta (2015), "Historic Developments, Current Technologies and Potential of Nanotechnology to Develop Next Generation Solar Cells with Improved Efficiency".
- [21] Ying, G., *et al.* (2009), "Profiling innovation system for Solar Photovoltaics in China", *Industrial Engineering and Engineering Management*, IEE IEEM, 2009.
- [22] Zhao, X., *et al.* (2015). "Distributed solar photovoltaics in China: Policies and economic performance." *Energy* 88: 572-583.

- [23] Wilkinson, S. and Jin, J. (2016), "PV Integrated Market Traker-Q4 2015", IHS Technology.
- [24] Khan, J. and M. H. Arsalan (2016). "Solar power technologies for sustainable electricity generation – A review." *Renewable and Sustainable Energy Reviews*, Elsevier, 55: 414-425.
- [25] Bharti, R., *et al.* (2009), "Nominal Operating Cell Temperature (NOCT): Effects of module size, loading and solar spectrum.", *Photovoltaic Specialists Conference (PVSC)*, IEEE.
- [26] Chander, S., *et al.* (2015). "Impact of temperature on performance of series and parallel connected mono-crystalline silicon solar cells." *Energy Reports* 1: 175-180.
- [27] Qasem, H., *et al.* (2014). "Dust-induced shading on photovoltaic modules." *Progress in Photovoltaics: Research and Applications* 22(2): 218-226.
- [28] Xiao, S. and S. Xu (2014). "High-Efficiency Silicon Solar Cells—Materials and Devices Physics." *Critical Reviews in Solid State and Materials Sciences* 39(4): 277-317.
- [29] Zhao, J., *et al.* (1998). "19.8% efficient "honeycomb" textured multicrystalline and 24.4% monocrystalline silicon solar cells." *Applied Physics Letters* 73(14): 1991-1993.
- [30] Blakers, A., *et al.* (2013). "High Efficiency Silicon Solar Cells." *Energy Procedia* 33: 1-10.
- [31] Tang, Z., *et al.* (2015). "Fully-solution-processed organic solar cells with a highly efficient paper-based light trapping element." *J. Mater. Chem. A* 3(48): 24289-24296.
- [32] ABB (2010), "Technical Application Papers No.10 Photovoltaic plants".
- [33] Horne, S. (2012). 10 - Concentrating photovoltaic (CPV) systems and applications. *Concentrating Solar Power Technology*, Woodhead Publishing: 323-361.
- [34] Peng, J., *et al.* (2013). "Review on life cycle assessment of energy payback and greenhouse gas emission of solar photovoltaic systems." *Renewable and Sustainable Energy Reviews* 19: 255-274.
- [35] Liu, X., *et al.* (2015). "Lifecycle climate impacts and economic performance of commercial-scale solar PV systems: A study of PV systems at Nevada's Desert Research Institute (DRI)." *Solar Energy* 119: 561-572.
- [36] Mekhilef, S., *et al.* (2012). "Effect of dust, humidity and air velocity on efficiency of photovoltaic cells." *Renewable and Sustainable Energy Reviews* 16(5): 2920-2925.
- [37] Mani, M. and R. Pillai (2010). "Impact of dust on solar photovoltaic (PV) performance: Research status, challenges and recommendations." *Renewable and Sustainable Energy Reviews*, Elsevier Journal, 14(9): 3124-3131.
- [38] Piliouline, M., *et al.* (2013). "Comparative analysis of energy produced by photovoltaic modules with anti-soiling coated surface in arid climates." *Applied Energy* 112: 626-634.
- [39] Sarver, T., *et al.* (2013). "A comprehensive review of the impact of dust on the use of solar energy: History, investigations, results, literature, and mitigation approaches." *Renewable and Sustainable Energy Reviews* 22: 698-733.
- [40] Kawamoto, H. and T. Shibata (2013), "Electrostatic cleaning system for removal of sand from solar panels", *Photovoltaic Specialists Conference (PVSC)*, IEEE 39th.
- [41] Satas, D. and A. Tracton, (2001), "Coatings Technology Handbook", Second Edition, Marcel Dekker, Inc., New York.
- [42] Koleske, J., V. (2006), "Mechanical Properties of Solid Coatings", John Wiley & Sons.
- [43] Yao, L. and J. He (2014), "Recent progress in antireflection and self-cleaning technology – From surface engineering to functional surfaces." *Progress in Materials Science* 61: 94-143.
- [44] Parkin, I. P. and R. G. Palgrave (2005), "Self-cleaning coatings." *Journal of Materials Chemistry* 15(17): 1689-1695.
- [45] Ragesh, P., *et al.* (2014), "A review on 'self-cleaning and multifunctional materials'." *Journal of Materials Chemistry A* 2 (36): 14773-14797.
- [46] Nishimoto, S. and B. Bhushan (2013), "Bioinspired self-cleaning surfaces with superhydrophobicity, superoleophobicity, and superhydrophilicity." *RSC Advances* 3(3): 671-690.

- [47] Kandlikar, S. G. *et al.* (1999), "Handbook of Phase Change: Boiling and condensation", Taylor & Francis.
- [48] Wang, T., *et al.* (2011). "Transparent nanostructured coatings with UV-shielding and superhydrophobicity properties." *Nanotechnology* 22(26): 265708.
- [49] Latthe, S. S., *et al.* (2009). "Superhydrophobic silica films by sol-gel co-precursor method." *Applied Surface Science* 256(1): 217-222.
- [50] Wang, S.-D. and Y.-Y. Shu (2013). "Superhydrophobic antireflective coating with high transmittance." *Journal of Coatings Technology and Research* 10(4): 527-535.
- [51] Xu, L., *et al.* (2014). "Mechanically Robust, Thermally Stable, Broadband Antireflective, and Superhydrophobic Thin Films on Glass Substrates." *ACS Applied Materials Interfaces* 6(12): 9029-9035.
- [52] Gao, L. and T. J. McCarthy (2006). "Contact Angle Hysteresis Explained." *Langmuir* 22(14): 6234-6237.
- [53] Liu, K., *et al.* (2010). "Recent developments in bio-inspired special wettability." *Chemical Society Rev* 39(8): 3240-3255.
- [54] Koch, K., *et al.* (2009). "Fabrication of artificial Lotus leaves and significance of hierarchical structure for superhydrophobicity and low adhesion." *Soft Matter* 5(7): 1386-1393.
- [55] Dorrer, C. and J. Ruhe (2007). "Condensation and Wetting Transitions on Microstructured Ultrahydrophobic Surfaces." *Langmuir* 23(7): 3820-3824.
- [56] Xiu, Y.H., Hess, D.W., Wong, C.R. (2008), "UV and thermally stable superhydrophobic coatings from sol-gel processing.", *J. Colloid Interface Sci.* 326 (2), 465-470.
- [57] Sinko, K. (2010). "Influence of Chemical Conditions on the Nanoporous Structure of Silicate Aerogels." *Materials* 3(1): 704.
- [58] Zhang, P. and F. Y. Lv (2015). "A review of the recent advances in superhydrophobic surfaces and the emerging energy-related applications." *Energy* 82: 1068-1087.
- [59] Aliofkhaezraei, M. (2011), "Nanocoatings: Size Effect in Nanostructured Films", Berlin, Springer Science and Business Media.
- [60] C. J. Brinker and G. W. Scherer (1990), "Sol-gel science: the physics and chemistry of sol-gel processing", Boston, Academic Press.
- [61] Li, X. and J. Shen (2013). "Deforming water droplets with a superhydrophobic silica coating." *Chemical Communications* 49(85): 10016-10018.
- [62] R. K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, New York, John Wiley & Sons.
- [63] A. C. Pierre (1998), "Introduction to sol-gel processing", Berlin, Springer Science and Business Media.
- [64] J. D. Wright and N. A. Sommerdijk (2000), "Sol-gel Materials: Chemistry and Applications", CRC Press.
- [65] Xunzel, SOLARTHINTM Series (2016), Available from: <<http://www.xunzel.com/portu/assets/xunzel-solarthin-portu-tz.pdf>> (retrieved 25.02.16).
- [66] McKeen, L. W. (2016). "10 - Application of Liquid Coatings. Fluorinated Coatings and Finishes Handbook (Second Edition)". Oxford, William Andrew Publishing: 171-183.
- [67] Hench, L. L. and J. K. West (1990). "The sol-gel process." *Chemical Reviews* 90(1): 33-72.
- [68] Tracton, A. A. (2007), "Coatings Technology- Fundamentals, Testing, and processing Techniques" (3rd ed.), CRC Press.
- [69] Wu, Q., Merchant, F. and Castleman, K. R. (2008), "Microscope Image Processing" (3rd ed.), Elsevier.

- [70] Goldstein, J. *et al.* (2003), "Scanning Electron Microscopy and X-Ray Microanalysis" (3rd ed.), Kluwer Academic.
- [71] Skoog, D. A., *et al.* (2004), "Fundamentals of Analytical Chemistry" (8th edition), Thomson Brooks/Cole.
- [72] Abdulrazzaq, O. A., *et al.* (2013). "Organic Solar Cells: A Review of Materials, Limitations, and Possibilities for Improvement." *Particulate Science and Technology* 31(5): 427-442.
- [73] Singh, L. P., *et al.* (2014). "Sol-Gel processing of silica nanoparticles and their applications." *Advances in Colloid and Interface Science* 214: 17-37.
- [74] Schaeffer, D. A., *et al.* (2015). "Optically transparent and environmentally durable superhydrophobic coating based on functionalized SiO₂ nanoparticles." *Nanotechnology* 26(5): 055602.
- [75] Gao, L. and J. He (2013). "A facile dip-coating approach based on three silica sols to fabrication of broadband antireflective superhydrophobic coatings." *J Colloid Interface Science* 400: 24-30.
- [76] Gao, Y. Q., *et al.* (2014). "Highly Transparent and UV-Resistant Superhydrophobic SiO₂-Coated ZnO Nanorod Arrays." *ACS Applied Materials Interfaces* 6(4): 2219-2223.
- [77] Liu, Y., *et al.* (2012). "Robust, Novel, and Low Cost Superhydrophobic Nanocomposites Coating for Reliability Improvement of Microelectronics." 2012 IEEE 62nd Electronic Components and Technology Conference (ECTC): 2135-2139.
- [78] Oko, C., *et al.* (2012). "Design and Economic Analysis of a Photovoltaic System: A Case Study. ", *International Journal of Renewable Energy Development* 1 (3):65–73.
- [79] Boubault, A., *et al.* (2016). "Levelized cost of energy (LCOE) metric to characterize solar absorber coatings for the CSP industry." *Renewable Energy* 85: 472-483.
- [80] Martifer Solar, Algarve Projects Case Study. Available from:<http://www.martifersolar.com/downloads/case_studies/web_CaseStudy_AlgarveProject.pdf>(retrieved 09.01.15).
- [81] Martifer Group, Being Global, Relatório e Contas 2012 (in Portuguese). Available from:<http://www.martifer.com/fotos/publicacoes/relatoriocontas2012_1726983320516c2304bcee8.pdf>(retrieved 09.01.15)
- [82] Decree-Law 35 from Diário da República, 1st serie- N°42- February 28th of 2013 (in Portuguese).