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Electrochemical Production of Self-standing TiO_2 Membranes for Advanced Water Purification

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MATERIALS ENGINEERING AND NANOTECHNOLOGY -
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Abstract

Water scarcity is one of the most pressing challenges facing modern society, as climate change and environmental pollution are increasingly stressing global freshwater resources. In this context, the focus of the scientific community is shifted towards the development of novel energy-efficient technologies for advanced water purification.

Under these conditions, the COPE project proposed an innovative interfacial solar evaporator based on photocatalysis for clean water production free from organic contaminants. This thesis aimed to investigate the fabrication and photocatalytic performance of free-standing TiO_2 nanotubular membranes that will be integrated into such systems.

TiO_2 nanotubular layers were synthesized either through a multi-step electrochemical oxidation under galvanostatic conditions or via a single-step potentiodynamic anodization process. Visual characterization tests were conducted after each anodization step to assess the formation of defects and the structural integrity of the oxide layer. The outcomes from these experiments evidenced that electrolyte aging, through variations of pH value, temperature, and viscosity, promotes non-uniform morphologies and a fragile structure. These findings highlight the importance of electrolyte management to guarantee the reproducibility and reliability of the synthesis process.

Photocatalytic degradation tests confirmed the ability of TiO_2 , both as free-standing membranes and anodized Ti substrate, to degrade the organic dye present in aqueous solution. In the final part of the thesis work, additional photocatalytic experiments were carried out to analyze the enhancement in photodegradation activity achieved by loading titania nanotubes with semiconductor quantum dots through the drop-casting technique. The improvement is attributed to the synergistic interaction between the photocatalyst and the photoabsorber when both are implemented in the same system. The results confirmed the enhancement in photocatalytic performance for both membranes and anodized substrates functionalized with core-shell and core-only quantum dots.

Keywords: Solar water evaporators; titanium dioxide; anodization; photocatalysis; nanotubes; semiconductor quantum dots.

Abstract in lingua italiana

La scarsità d'acqua è uno dei problemi più urgenti che affliggono la società moderna, poiché il cambiamento climatico e l'inquinamento ambientale deteriorano ulteriormente le risorse idriche globali. In questo contesto, l'attenzione della comunità scientifica è incentrata sullo sviluppo di tecnologie innovative a basso consumo energetico per la depurazione avanzata dell'acqua.

Seguendo queste condizioni, il progetto COPE ha proposto un evaporatore solare interfacciale moderno basato sulla fotocatalisi per la produzione di acqua potabile senza inquinanti organici. L'obiettivo di questa tesi era di analizzare la realizzazione e il comportamento fotocatalitico di membrane nanotubulari autoportanti di biossido di titanio che verranno integrate in questi sistemi.

Gli strati nanotubulari di biossido di titanio sono stati sintetizzati tramite ossidazione elettrochimica multifase in condizioni galvanostatiche oppure mediante anodizzazione potenziodinamica a singolo stadio. Sono state effettuate verifiche visive dopo ogni singola anodizzazione per controllare la formazione di difetti e l'integrità strutturale. Gli esiti di questi esperimenti hanno evidenziato come l'invecchiamento dell'elettrolita possa promuovere la crescita di geometrie non uniformi e di strutture fragili attraverso variazioni nel valore del pH, nella temperatura e nella viscosità. Questi risultati dimostrano l'importanza della supervisione dell'elettrolita per garantire un processo di sintesi riproducibile e affidabile.

Le prove di degradazione tramite fotocatalisi hanno confermato la capacità del biossido di titanio, sia in forma di membrana autoportante che di strato di titanio anodizzato, nel degradare un colorante organico misciato in una soluzione acquosa. Nella parte finale di questa tesi, ulteriori esperimenti sulla fotocatalisi sono stati condotti per analizzare il miglioramento nell'abilità di fotodegradazione ottenuto dopo aver applicato sui nanotubi di titanio dei quantum dots tramite tecnica di deposizione a goccia. Questo potenziamento è dovuto all'interazione sinergica tra il fotocatalizzatore e il materiale fotoassorbente quando entrambi vengono implementati nello stesso sistema. I risultati hanno confermato l'ottimizzazione del processo di fotocatalisi sia per le membrane che per gli strati anodizzati dopo l'introduzione di quantum dots di tipo core-shell e core-only.

Parole chiave: Evaporatori solari; biossido di titanio; anodizzazione; fotocatalisi; nanotubi; quantum dots semiconduttori.

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1 | State of the art

1.1. State of water

Water availability and its management are fundamental requirements for human health and sustainable development. However, according to a report compiled by the Food and Agriculture Organization in 2020, approximately 3.2 billion people live in agricultural areas with high to very high water shortages or scarcity.

Water shortages are determined by inadequate rainfall patterns that lead to a lack of water of acceptable quality, and climate change plays an important role, as it is associated with more severe droughts. Climate change impact is also expected to increase the risk of other extreme weather events like floods and climate variability, which will negatively affect the agricultural production of tropical regions and freshwater ecosystems that are sensitive to the latter effect. Thus, climate change will put water resources under increasing stress over time. From water shortages arises water scarcity, as well as from other factors driving water demand, like population increase. In particular, the rapid population growth has determined a decrease in the amount of annual freshwater per person by more than 20% in the last decades.

As shown in Figure 1.1, many countries are highly water stressed but while high-income nations in Europe and Northern America have a greater capacity to address this challenge, in regions located in Northern Africa and Asia where the same areas can experience water stress and high drought frequency, due to the lower levels of agricultural capital investments farmers have difficulty in accessing modern irrigation equipment and technologies to optimize the efficiency of water use [1].

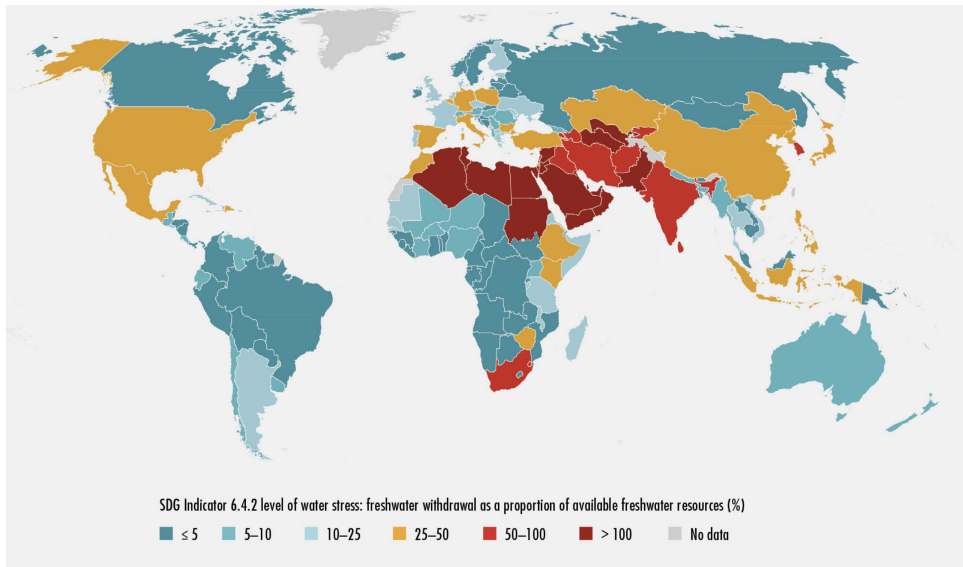


Figure 1.1: Level of water stress at country level, 2015 [1].

1.2. Organic pollutants and salinity issues

The main cause of environmental pollution is human activity, by means of industrialization and urbanization, that determine the release of hazardous chemicals and solid wastes into the ecosystem. The presence of pollutants in water brings the emergence of waterborne diseases like cholera and typhoid fever, and it is estimated that 10-20 million people die every year due to waterborne pathogens [40]. Apart from pesticides, whose presence is caused by agricultural discharge, four other main pollutants contaminate the quality of freshwater:

- Heavy metals. These compounds are mainly concentrated around mining and industrial areas, but they can also be released into the environment by natural events.
- Hydrocarbons. These substances include all the polycyclic aromatic hydrocarbons, and their presence is largely due to incomplete combustion of organic matter as well as waste from industrial processes.
- Halogenated hydrocarbons. This group consists of organic solvents, flame retardants, and dioxins. They are classified according to their origin, which can be natural in the case of halogenation reactions occurring during the incineration of biomass, or synthetic, like residues from industrial chemical reactions.
- Alkylphenols. Their major problem is their tendency to accumulate due to their extensive usage as precursors for detergents, as additives for fuels, and as components for phenolic resins [41].

Considering the presence of all these pollutants in natural freshwater resources and their rapid depletion, seawater is emerging as a non-traditional source of safe drinking water. However, while the presence of organic contaminants remains a major challenge for human consumption, high levels of salinity pose another critical issue when dealing with marine water. Among the conventional technologies, reverse osmosis has been widely adopted over the years for reliable seawater desalination.

1.3. Reverse osmosis

The main process of reverse osmosis is based on an osmotic membrane, a dense and thick barrier whose function is the separation of components, in this case, salts, by means of a solution-diffusion mechanism. Figure 1.2 offers an illustration of the traditional steps in a reverse osmosis desalination plant.

It starts with a pre-treatment process to eliminate larger particles that can cause clogging if deposited onto the membrane. More in detail, this operation is mainly conducted by granular media filtration, where the filtration is achieved through the adsorption of suspended particles on top of sand or anthracite grains.

Then, the feed water arrives at the core of the plant, a semi-permeable layer able to filter water molecules while blocking heavier ones. However, the osmotic pressure generated from the concentration gradient between the seawater and the treated water acts as a barrier to the filtration of water. In order to solve this problem, a high-pressure pump is implemented before the reverse osmosis system.

At last, desalinated water flows through a post-treatment step to remove any residual particles before obtaining drinkable freshwater. Meanwhile, due to the presence of a residual pressure in the dense phase retained by the membrane, before being discharged, the brine is transported to an energy recovery device where this pressure energy is recovered to pressurize the input stream. This process greatly reduces the specific energy consumption of the plant. Nonetheless, the recycled pressure isn't sufficient, and so the feed stream is also aided by a buster pump [2].

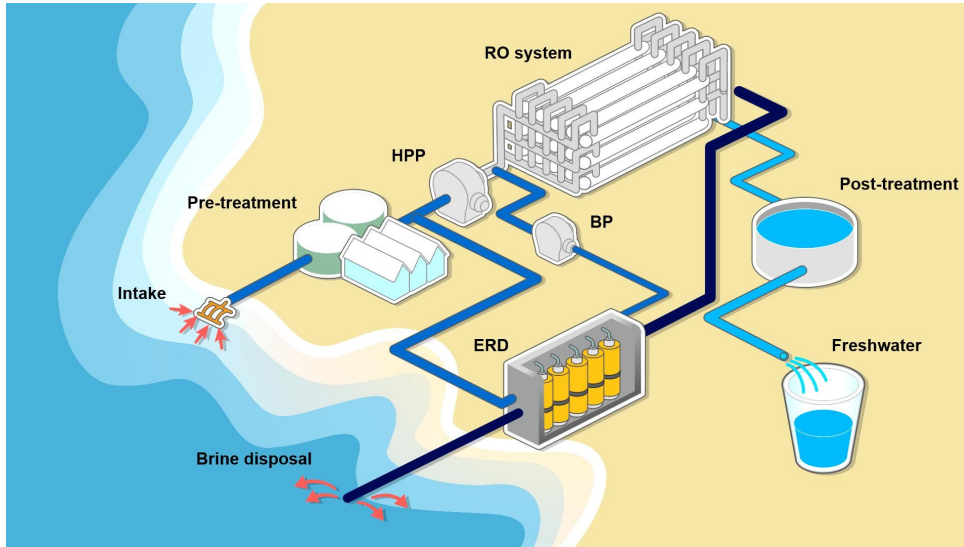


Figure 1.2: Scheme of a reverse osmosis desalination plant [2].

1.3.1. Limitations of reverse osmosis

Despite the introduction of devices to recover part of the power demand of the plant and the advances in membrane technology, reverse osmosis desalination is still the most energy-intensive option for the supply of potable water from seawater. More in detail, the reverse osmosis system covers 71% of the total plant energy use, while the pre-treatment step only 10.8% [42]. As seen in the previous paragraph, these numbers can be justified by the significant amount of energy needed to overcome the osmotic pressure exerted over the membrane.

In recent years, the world has seen a drastic increase in the number and size of desalination plants since more governments are leaning towards seawater to face the pressure from population growth and water shortages. However, due to the high-energy consumption of the process, this global trend has determined a significant increase in the demand for fossil fuels and other non-renewable energy sources, which may lead to serious damage to the environment. Indeed, their excessive usage can establish an escalation of the greenhouse gases emitted from the factory, which will negatively impact climate change [43].

Consequently, future improvements in seawater desalination plants will be focused to reach a sustainable seawater management.

1.4. Introduction to solar evaporators

1.4.1. Solar water evaporation

Conventional water treatments such as reverse osmosis suffer from their limit of high energy consumption and, despite the ongoing research to solve this problem, the crisis coming from water shortage pushes the development of new devices for water desalination and decontamination urgently.

Recently, many scientists have focused their attention on solar water evaporation as a feasible solution since solar radiation represents a considerable and renewable energy source for the sustainable development of our society. This system works by absorbing solar energy and converting it into heat to accelerate the evaporation of seawater or wastewater. Then, steam is collected in solar stills, where it is condensed to generate potable water. These solar stills are capable of providing drinkable water during emergencies and in remote locations, while also being an economically viable option to agricultural wastewater treatment compared to conventional strategies [44]. Further research has showcased the potential to extend the range of this technology beyond water purification, covering fields like energy generation [45].

1.4.2. Solar-driven interfacial evaporators

Traditionally, solar water evaporators require a photo-thermal absorber, characterized by high solar absorption and conversion efficiency, placed at the bottom or evenly dispersed in water, leading to a significant amount of heat loss during the solar-thermal conversion process. A viable solution has been proposed with systems based on interfacial evaporation, where the device floats above the water surface on a porous, hydrophilic layer.

With this new design, solar evaporators have gained a renewed interest due to the localization of photo-thermal conversion to the evaporating interface, so excluding the bulk water, which allowed the minimization of heat loss and enhanced energy transfer efficiency with the aid of the floating layer for thermal insulation [45]. Figure 1.3 illustrates a generic configuration of a solar evaporator based on interfacial heating distillation, while a more detailed description of the absorber and porous support will be given in the next sections.

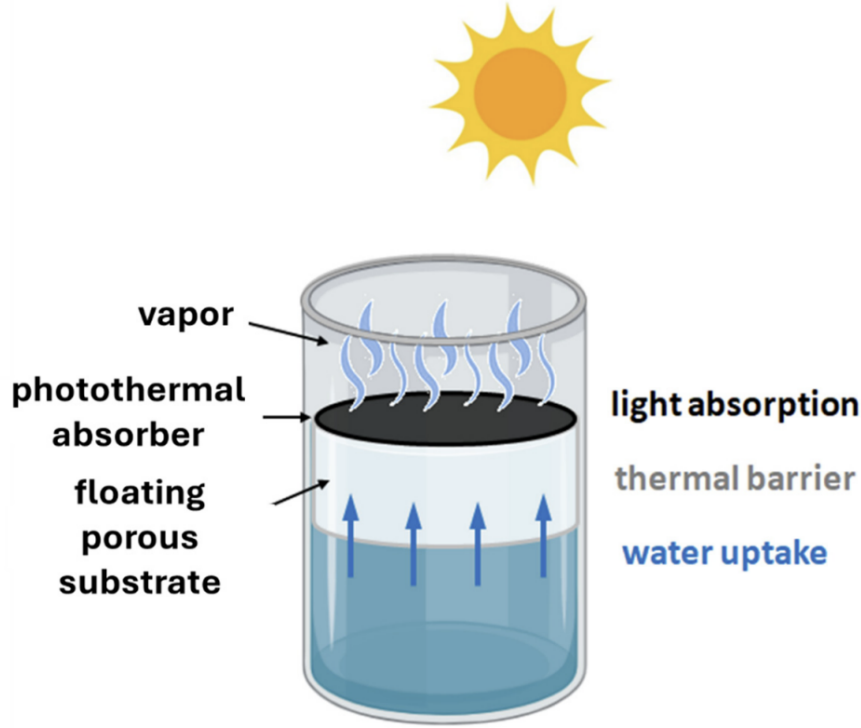


Figure 1.3: Generic configuration of an interfacial solar evaporator.

1.5. Photo-thermal absorbers

Photo-thermal materials play a key role in evaporators as the elements in control of solar harvesting in the system. Therefore, scientists have developed advanced solar absorbers based on different materials in order to enhance light absorption and the generation of heat. Indeed, material selection and composition tunability play a fundamental role in achieving high solar absorbance while limiting heat losses during the photo-thermal conversion due to the arising of conduction, convection, and radiation phenomena. Scientists have recognized three critical criteria for engineering suitable solar absorber materials:

- **Efficient light absorption.** An optimal light-harvesting ability of the material requires high absorption along the entire solar spectrum, ranging from 300 nm up to 2500 nm of wavelength (according to the AM 1.5 standard), with very low transmittance and reflectance so as to maximize the conversion of the energy coming from the sun. Indeed, a high solar to thermal efficiency needs a high solar absorptance, a quantity introduced to evaluate the fraction of solar radiation absorbed given a specific angle of incidence θ . This variable is measured as the ratio of the material's spectral absorbance over the spectral irradiance distribution of the standard solar spectrum, integrating along the wavelength range of the radiation reaching the ma-

terial surface. After normalizing the value to the total solar irradiance, the complete formula for the total solar absorptance $\alpha(\theta)$ of a solar absorber is obtained:

$$\alpha(\theta) = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} [1 - R(\theta, \lambda)] A(\theta, \lambda) d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} A(\lambda) d\lambda} \quad (1.1)$$

where the angle of incidence θ is detected from the axis normal to the surface of the absorber, $\lambda_{\max}$ and $\lambda_{\min}$ are the maximum and minimum wavelengths of the solar spectrum range, $A(\lambda)$ is the solar spectral irradiance while $R(\theta, \lambda)$ is the overall reflectance for a specific wavelength [46].

- Capable solar conversion mechanism. Light-to-heat conversion is a pivotal element for a solar absorber since, ideally, the process should transform all the energy coming from the sun without radiative losses. The photothermal efficiency is a parameter introduced to quantify this conversion, and in many experiments it is measured directly by evaluating the rise in temperature of a solution containing the solar absorber under light irradiation and the corresponding heat energy generated [47, 48]. In these laboratory tests, the light source is typically a laser while the gold nano-materials are in charge of the photothermal conversion. Through a thermocouple, scientists are able to monitor the temperature profile of the solution, detecting the increase caused by heat energy coming from the absorber material. Finally, the conversion efficiency is then determined by comparing the heat energy gained by the system, excluding losses from conduction and radiative phenomena, and the laser extinction power.
- Reliable heat regulation for steam generation. In order to maximize the vaporization efficiency, all the energy generated from the light-to-heat conversion should be used to overcome the latent heat of evaporation of water while keeping the conduction, convection, and radiation mechanisms to a minimum. In reality, these processes that lead to unproductive heat consumption are inevitable. Steam generation efficiency is experimentally measured with a setup similar to the ones for the evaluation of the photothermal efficiency; however, in this scenario, the light source power input is compared with the mass loss of the solution against time. The overall efficiency η is calculated with the following formula:

$$\eta = \frac{m(L_v + Q)}{P_{\text{in}}} \quad (1.2)$$

where m is the water evaporation rate, L_v refers to the latent heat of evaporation which is also a constant for each specific temperature range, Q represents the en-

ergy required to raise the temperature of the system to the required value and P_{in} corresponds to the light power density incident on the material [3, 49].

Other important properties to consider when selecting the best solar absorber material are scalable and reproducible production methods, its economic viability, and the durability of the device. Taking into account all these variables, researchers have narrowed down the potential candidates into the following classes [3, 46].

1.5.1. Inorganic semiconductor-based absorbers

Semiconducting materials are characterized by spontaneous thermalization, which can be exploited to generate heat localized on the surface. Under appropriate light irradiation with an energy similar to the band gap, the excited electrons jump from the valence band to the conduction one leaving behind a hole. Thus, an electron-hole pair is formed, and it is called an exciton. Eventually, the electrons return to the lower level by releasing their energy in the form of photons; this process is called radiative recombination. In case of non-radiative recombination, energy is transferred in the form of phonons to lattice defects or dangling bonds present at the surface of the material, as shown in Figure 1.4b. This process generates a local heating of the lattice and a temperature gradient that is influenced by the optically excited diffusing and recombining carriers. However, some of the generated heat is emitted, determining a reduction of its localization. In order to improve the efficiency of the process, scientists have resorted to doping and surface modification of the semiconductor. Nanostructured copper sulfides have proven to be reliable solar absorbers because of their strong solar absorption, low production cost, and fast photo-thermal conversion. Moreover, many other semiconducting materials, such as metal oxides and composite materials, are being considered because of their high water evaporation efficiencies [46, 49].

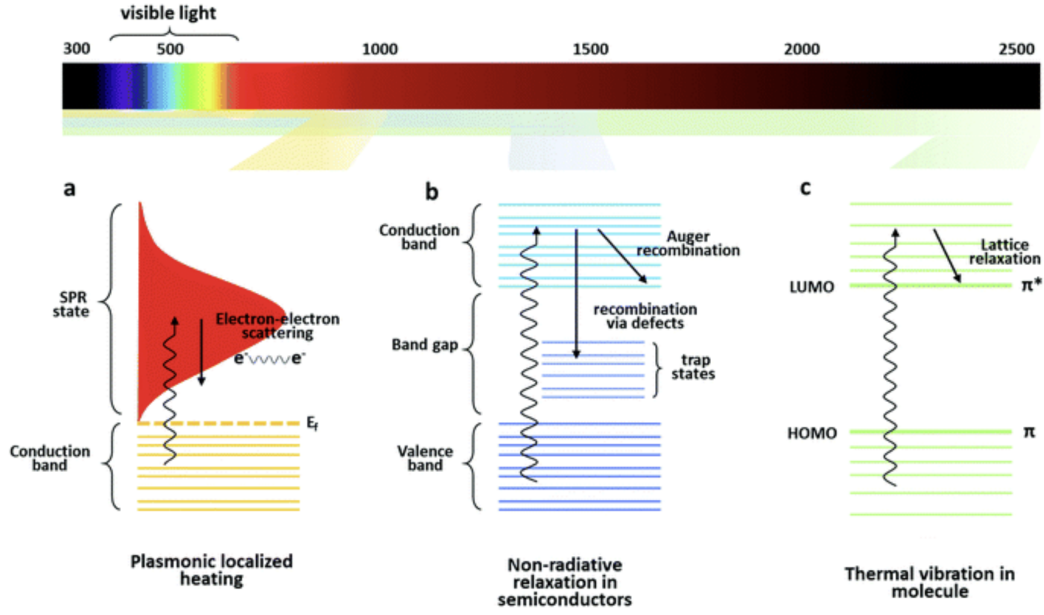


Figure 1.4: Different mechanisms of the photo-thermal effect with the corresponding light absorption range [3].

1.5.2. Surface plasmon resonance metals

When nanoparticles made of noble metals like gold or silver are irradiated with photons of frequency equal to the natural frequency of surface electrons, a resonant photon-induced coherent oscillation of charges is induced. This phenomenon is called localized surface plasmon resonance, and it triggers three sequential processes, namely near-field enhancement, hot electron generation, and photo-thermal conversion. Essentially, when electrons are irradiated at their resonance wavelength, the electron gas starts to oscillate, and the electrons are excited from the occupied state to the unoccupied ones, becoming hot electrons. Their decay can occur through radiative relaxation or electron-electron scattering. In the latter case, depicted in Figure 1.4a, the energy is redistributed in the form of heat that leads to an increase in the temperature at the surface of the nanoparticles. Following this, the energy of electrons is transferred to lattice phonons, and finally, heat is dissipated in the surrounding medium by phonon-phonon interactions, determining a rise in the local temperature of the system. This effect is strictly correlated to the shape and size of the surface plasmon absorption band since the plasmon resonance energies regulate the energy of the hot electrons generated. While many studies have demonstrated the validity of the plasmonic photo-thermal effect in solar absorbers, the research is still in an early stage since, a few decades ago, the heat generation by plasmonic nanoparticles was considered a side effect [3].

1.5.3. Organic polymers

Polymers can absorb optical energy and convert it into heat by means of lattice vibration (Figure 1.4c). This mechanism can be exploited by the presence of π electrons that can be excited with a lower energy input compared to σ electrons. Indeed, in σ bonds, the carriers are more strongly bonded and require photons with lower wavelength to jump to higher energy levels. Meanwhile, many organic materials constituted by long π -conjugated molecules are characterized by a red-shift in the absorption spectrum since the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is smaller. The more extended the π -conjugation is, the higher the wavelength associated with the transition of the electrons in the LUMO is, shifting towards the visible and infrared regions. This correlation explains why in polymers with a large quantity of π conjugated bonds, electrons can be excited by photons with almost every wavelength in solar light irradiation [49]. The photo-heat conversion happens when the photo-excited electrons relax by means of electron-phonon couplings, where the absorbed energy is transferred to vibrational modes throughout the atomic lattices, leading to a macroscopical increase in the temperature of the material [50]. From a practical point of view, polymers can also work as floating support owing to their ability to increase the immobilization of solar absorbers and by strengthening their affinity with different supports like wood [46].

1.5.4. Carbonaceous materials

Carbon-based solar absorbers such as graphene, carbon dots, and carbon nanotubes proved to be very efficient and with low production cost. Indeed, compared to conventional solar-driven steam generators, the water evaporation process occurs in a matter of seconds upon irradiation, which is attributable to the fast release of energy via electron relaxation. Moreover, these systems possess an extended conjugation of π bonds that, as discussed in the previous section, results in an enhanced solar light absorption response, in other words, an improved generation of heat. With respect to metals and semiconductors, carbon-based materials are also more affordable and widely available. The main issue related to this class of solar absorbers is the absence of a comprehensive analysis and a limited understanding of the fundamental principles regarding carbon material design for steam generation. Therefore, while many articles are being published every year, communication in the scientific community is the key to achieving further progress in this field [3, 51].

1.5.5. Semiconductor quantum dots

Semiconducting nanocrystals are considered encouraging light-harvesting materials, and nowadays they are widely applied in many fields such as photovoltaics, sensing technology, and medicine. In addition to the interesting electrical and optical properties of semiconductors, the architecture at the nanometer scale offers an additional advantage: the size-dependent behavior of the electronic states. This is a consequence of the quantum confinement, where the electrons are restrained in a domain smaller than their de Broglie wavelength. As the feature size of the dots decreases, the gap between the valence and conduction bands increases, leading to a blue shift of the absorption spectra. Over the years, scientists designed nanocrystals whose light absorption can be finely tuned over the entire solar spectrum, across both the visible and IR regions [52]. Traditionally, the methods to fabricate quantum dots are divided into two main strategies: physical vacuum-based epitaxial techniques and wet-chemical approaches.

Moreover, the sensitivity of the dots to the environment can be manipulated through specific surface chemistry. Nowadays, colloidal quantum dots can be engineered with a surface ending with molecules or ions of different functionalities for a specific application. In particular, this class of nanomaterials consists of core-shell heterostructures, in which a core is covered with a nanocrystal shell. This strategy ensures the protection of the photoactive core against photodegradation in order to improve its stability. Core-shell quantum dots can be classified into three configurations depending on the relative band gap of the core and the shell, and the best one to act as a photoabsorber is type 3, where the gap between the conduction and the valence band is narrower in the outer material compared to the inner core. Here, the photogenerated electron-hole couples are present more dominantly near the surface of the shell material, thus accelerating the non-radiative recombination phenomena in order to minimize light emission and focus all the energy absorbed into heat generation. It has been implied that the absorption strength and spectrum can be finely tuned with the shell thickness. Indeed, as observed with homogeneous quantum dots, over the years, scientists were able to manipulate the composition and size distribution of a core-shell nanocrystal population to accomplish an absorption range which covers most of the solar spectrum, as highlighted in Figure 1.5.

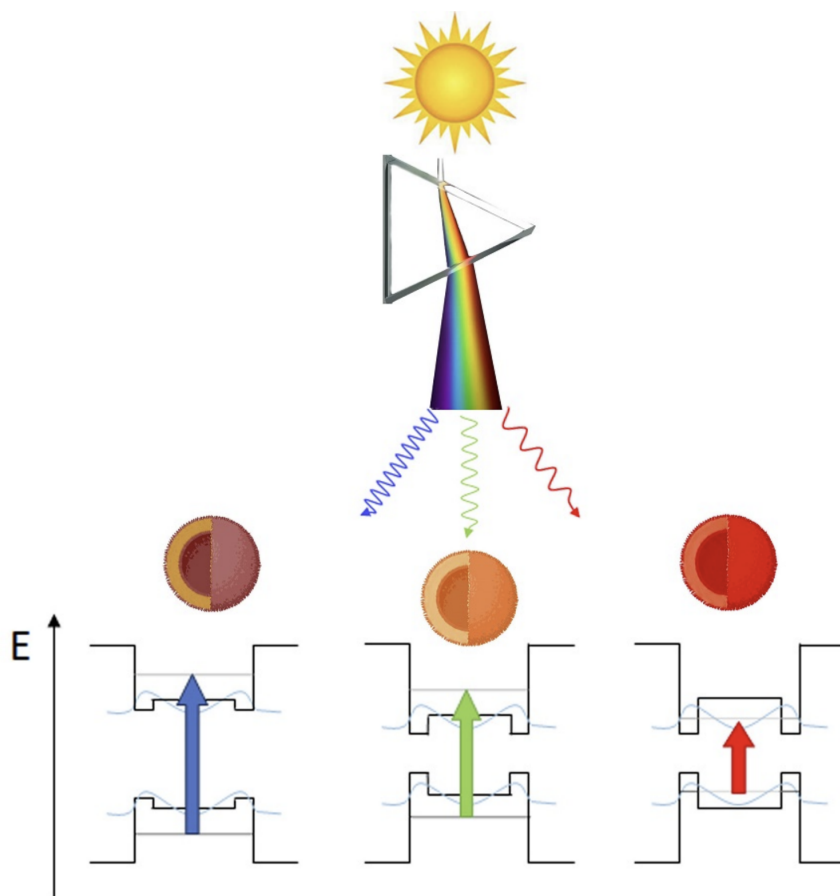


Figure 1.5: Schematic representation of cumulative light absorption over the entire spectrum achieved through careful composition and size distribution of the nanoparticle population.

While the core follows the classical methods of dots development, for the synthesis of the shell, scientists usually resort to colloidal atomic layer deposition. Following this approach, scientists were able to easily engineer the optical properties of the nanocrystals, achieving a narrow size distribution and shape homogeneity. Another useful aspect is the possibility to grow the shell at room temperature with high reproducibility for large-scale production. The results in the laboratories confirmed tunable intensity of the absorption spectra while varying the thickness of the shell [53]. Interestingly, this method proved to be extended to the combination of materials with different properties and lattices, like metal over a semiconductor, proving its flexibility and encouraging further research on this method.

1.6. Optimization of the floating substrate design

Along with the optical properties of the photothermal absorbers, the choices made in the structural design process play a key role in the overall system efficiency. Indeed, Figure 1.6a illustrates a bilayered structure where the solar absorber constitutes the top layer and is in charge of the light-to-heat conversion, while the bottom layer keeps heat losses to a minimum in addition to preventing any material dispersion into the bulk water. Another important characteristic of this framework is the presence of micropores in order to deliver water efficiently from the bulk to the evaporation zone. The first example of a double-layer structured interconnected porous evaporator consisted of an exfoliated graphite layer on top of a carbon foam template (Figure 1.6b). In this study, processed carbon foam exhibited acceptable thermal insulating properties as well as a hydrophilic character, fundamental to enhance the capillary force and so bring water to the upper layer through small pores. Exfoliation of the graphite sheet at high temperatures enhanced the layer's hydrophilicity, facilitating the transport of water more efficiently. As a result, through capillarity, a thin film of water is formed on the surface of the graphite, which enhances the surface area for evaporation and the formation of the three-phase contact lines at the boundaries of the capillaries. This system, initially proposed to solve the thermal localization problem of the photothermal devices, was able to achieve a solar-to-heat conversion efficiency of 85% at 10 kW m^{-2} of irradiance [4].

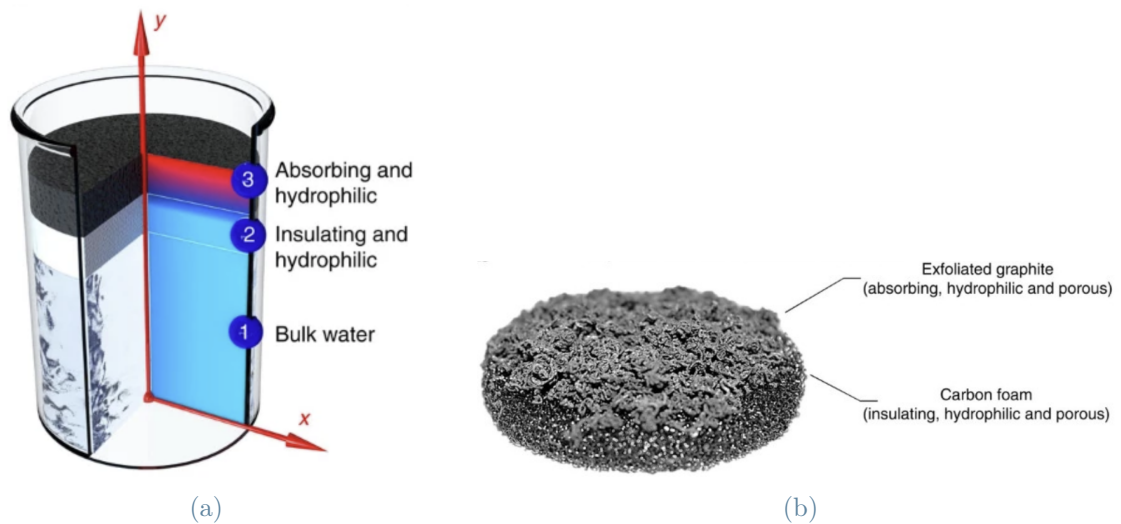


Figure 1.6: (a) Cross section of structure and temperature distribution of the first bilayered porous evaporators. (b) A picture under the microscope of the double-layer structure made of a carbon foam (10 mm thick) supporting an exfoliated graphite layer (≈ 5 mm thick) [4].

Following this study, evaporators with a porous bottom layer have become more widespread owing to their improvements in energy efficiency. In fact, new materials like airlaid paper, anodic aluminium oxide, silica, cellulose, and PVDF membranes have been selected in more recent experiments as the porous substrates for their insulating properties.

While the advantages of a bilayered structure have been widely demonstrated, scientists also explored new alternative designs over the years. In particular, some recent designs relies in the dispersion of photothermal particles onto a porous support, abandoning the structural idea of layer separation. Nonetheless, in these configurations, the porous scaffold still plays a key role in water transport and thermal localization. The main objective when designing these evaporators is the exploitation of the individual optical properties of the two materials in a synergic way to greatly enhance the overall absorption. For instance, Zhou et al. [5] reported a light absorbance of 99% within a broad range of wavelength from 400 nm to 10 μm . The absorber is manufactured from the sputtering of gold nanoparticles through physical vapour deposition on a nanoporous alumina layer with pores of different sizes. For a visual representation, Figure 1.7 shows the presence of gold nanoparticles with random dimensions that determine an increase of localized surface plasmonic resonant modes, which is essential to extend the absorption band of the system. Meanwhile, the nanoporous template characterized by a lower refractive index guarantees strong scattering and internal reflection for an extended light path inside the pores.

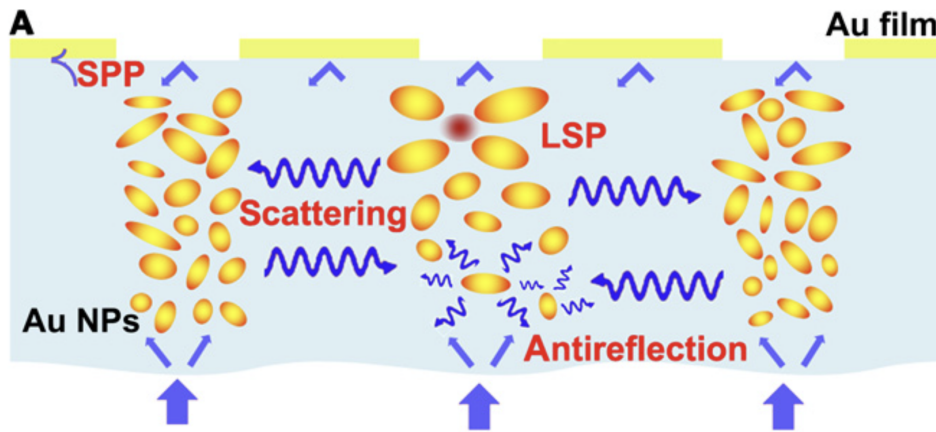


Figure 1.7: Schematic representation of a plasmonic absorber with Au nanoparticles on a nanoporous template [5].

In addition, this evaporator is a representative example of a hybrid system, a recent class of solar evaporation technology based on combinations of different materials, such as metal-organic structures and metal-semiconductor composites, which allowed scientists

to reach higher absorbance and photothermal conversion efficiency. Overall, there's no doubt that with further progress in the manufacturing process, this hybrid system, as well as others currently under development, will become more accessible in different fields like desalination and sensing technology.

1.6.1. Wood-based interfacial evaporators

In the optic of a more sustainable future, the transpiration of trees has inspired the implementation of natural wood as the substrate for photothermal materials. In nature, water travels from the roots of the plants through the channels inside the trunks towards the leaves to supply, and then it evaporates. Natural wood possesses a high density of vertically aligned microchannels and an interconnected network of pores for efficient water transportation (Figure 1.8a). When compared to the wavelength of light, the diameter of these channels is bigger, thus allowing wood to diffuse many wavelengths and increasing its absorption band. On the matter of the heat localization, experiments were conducted using a Steady State Laser-Infrared Camera for the characterization of heat transfer property, and they highlighted the low thermal conductivity of wood. In addition, during the comparison of different natural microstructures of carbonized wood, it has been reported that the more porous the system is, the higher the evaporation efficiency.

As a consequence of all of these advantages, as well as its abundance, natural wood is a perfect candidate as the supporting layer for interfacial solar evaporators, and many articles regarding this category have been published recently. Among them, Zhu et al. [7] developed a novel plasmonic wood for efficient steam generation by decorating wood with metal nanoparticles. After optical modeling of the system, scientists were able to ascertain a notable increase in the absorption property, reaching a stunning 99% in a broad wavelength range from 200 nm up to 2500 nm. This is the overall result of two phenomena, the plasmonic effect of the metal nanoparticles and the waveguide effect inside the microchannels of the wood matrix, which allowed the enhancement of light harvesting (Figure 1.8b).

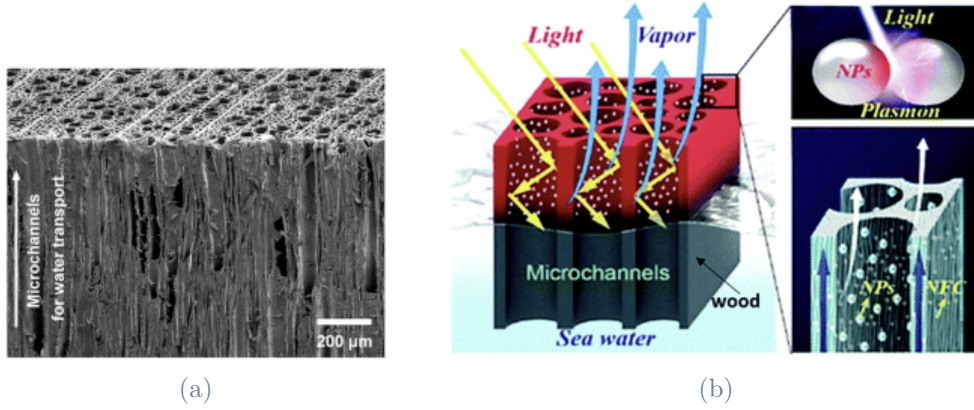


Figure 1.8: (a) SEM image of natural wood at 200 μm scale to reveal the microstructure consisting of longitudinally aligned microchannels and micropores in the cross-section [6]. (b) Scheme of plasmonic wood with the representation of the plasmonic effect of the metal nanoparticles and the waveguide effect inside the microchannels [7].

1.6.2. Solar absorber gels

Gels are examples of special photothermal materials that possess an intrinsic hierarchical structure of pores, and this condition allows them to be considered for the manufacturing of monolithic solar evaporators. The three-dimensional porous gel structure controls the thermal insulation, water supply, and the interfacial photothermal conversion without the assistance of an external floating substrate. Recently, Zhao et al. [54] realized an efficient solar vapor generator consisting of a hierarchically nanostructured gel (HNG) made of a hydrophilic network of polyvinyl alcohol (PVA) with dispersed polypyrrole (PPy) that acts as the solar absorber. Through SEM, scientists observed that after polymerization, the HNG exhibited a hierarchical network of water pathways with internal gaps, microchannels, and molecular meshes. This interpenetrating structure that mimics tree branches, thanks to the dispersion of the solar absorber in the gel, allows easier water evaporation in the meshes. Indeed, the energy coming from the conversion is directly transferred to the small quantity of water contained in the branches. The capillary action of the microchannels and internal gaps causes a continuous and fast water replenishment of the molecular meshes through dilation of the network, creating an efficient cycle able to sustain high evaporation rates. Zhao's group also reported a nullification of the convective heat losses due to the PVA chains, which is often regarded as the main cause of energy loss in interfacial solar vapor generators. Under natural sunlight, the documented evaporation rate values were double the conventional theoretical upper limit in the same environment. Another notable example is the solar absorber gel presented by Ho's group

[55]. In this system, solar absorbers gold nanoflowers, with high broadband absorption and efficient light-to-heat conversion, are sparsely dispersed in a porous silica gel characterized by low thermal conductivity. The overall structure establishes a macroscopic insulation to minimize thermal losses in bulk water, as well as a nanoscopic heat confinement near the nanoflowers. This efficient macro-nano thermal insulation facilitates the gel in retaining and delivering the heat directly to the water pathways inside the pores. With this design, scientists reported an evaporation efficiency of 85% under normal daylight. An important aspect of these examples, like many other monolithic solar absorber gels, is also their potential for scalable and less expensive manufacturing and the minimization of any incompatibility that may emerge at the surfaces of multilayered photothermal frameworks. Despite all these advantages, the low long-term stability of aerogels and polymers may hinder their future mass adoption. However, while the development of hybrid solar absorbers guarantees high evaporation rates, the smaller concentration of gel in these systems may lead to a loss of thermal insulation. Hence, for an efficient hybrid gel-based solar evaporator is fundamental to find an acceptable compromise between the choices for the solar absorber and the thermal insulator [46].

1.7. Technological issues in solar evaporators

While many milestones were achieved regarding the issue of thermal localization, other technological challenges still need to be solved for the purpose of implementing solar water evaporators in large-scale applications.

1.7.1. Salt accumulation

During the evaporation process of seawater, ion salts may precipitate at the water-air interface. Ideally, these ions should diffuse into the water cavity due to the difference in salt concentration between the evaporator surface and the bulk water. However, in an environment characterized by high salinity and high light intensity that determines fast evaporation rates, the risk of salt accumulation is augmented, and when it reaches a saturation value, salt crystallization occurs. These piled-up crystals will obstruct the pores of the structure, hindering the capillary effect and significantly limiting the evaporation process. For this reason, the salt-fouling issue in porous solar water evaporators must be addressed. At present, operators commonly use a combination of acids and scale inhibitors to dissolve salts like carbonates and sulfates. Nevertheless, these chemicals discharged in high-salinity water pose a threat to marine life, so scientists are currently researching new strategies to tackle the salt scaling problem. Three distinct and efficient approaches have

been identified and will be discussed below: mechanical removal, shielding effect, and force-driven fluid flow (Figure 1.9).

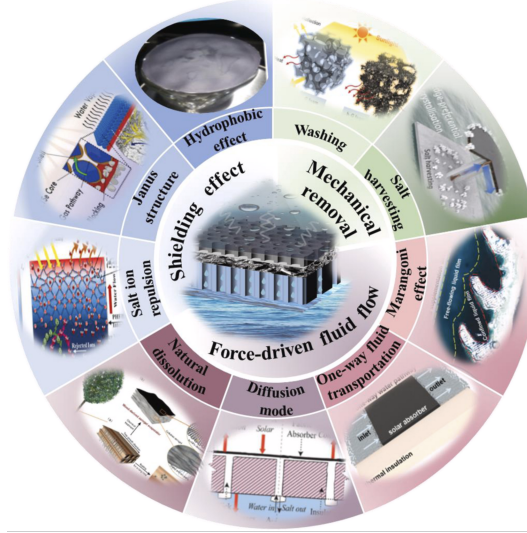


Figure 1.9: Scheme of the three principal salt elimination mechanisms [8].

Regarding the mechanical removal of salt, the simplest strategy to achieve this is through physical rinsing and washing operations after a long period of use. Mi et al.'s research group followed this strategy after reporting a significant salt accumulation on the evaporator surface [9]. With the purpose of enhancing the capability of solar evaporators to thrive even in high salinity waters, they aimed to replicate the salt filtration process of mangrove trees. In the first part of their project, Mi's group realized a hydrophilic synthetic leaf made of thin graphene oxide as the solar evaporator and placed it above water-based solutions with different $NaCl$ concentrations. After hours of exposure under light, they observed the formation of salt crystals with dimensions reaching a few centimeters after 5 days (Figure 1.10a). Even though the evaporation rate wasn't particularly affected, these deposits were labeled as a potential risk for dust build-up and additional weight on the absorber. For this reason, the crystals were scraped off while the synthetic leaf was rinsed in deionized water shortly after. With this research, Mi et al. established a new type of solar evaporators for sustainable desalination of seawater; nevertheless, its necessity for manual cleaning typically calls for a suspension of the photothermal operations, and this inevitably has financial repercussions.

In view of this, ex-situ salt harvesting technology is a promising alternative since it allows the recovery of sea salt as a byproduct by default. Recently, Shi et al. designed a three-dimensional cup-shaped solar evaporator to resolve the high cost and energy-demanding issues of zero-liquid discharge desalination technology [10]. Owing to the elaborate de-

sign of the cup, manufactured from a silica/carbon/silica trilayered fibrous membrane for a nearly perfect evaporation efficiency, scientists were able to achieve the automatic separation of the light-absorbing surface from the crystallization surface. Indeed, while the photothermal structure produces vapor from the inner wall, on the outer surface, the growth of salt crystals was observed. Even more remarkable, Shi's group reported a stable and high water evaporation rate without any substantial losses even when treating a solution with 25 wt% of *NaCl* after long-term operation despite the appearance of some precipitates at the bottom of the cup after 24 h, as shown in Figure 1.10b.

Another noteworthy example of the crystallization surface isolation is the study conducted by Xia et al. [11]. Xia's group designed a horizontal evaporating disc with a vertical cotton thread at the centre for solution uptake (Figure 1.10c). Thanks to this configuration, it was possible to achieve a salt concentration gradient toward the edges of the disc and thus isolate the crystallization sites. Finally, by lowering the adhesion forces between the disc and the salt crystals, the latter spontaneously detached under the action of gravity. With these properties, scientists were able to achieve continuous steam generation and salt harvesting over 600 h of non-stop operation.

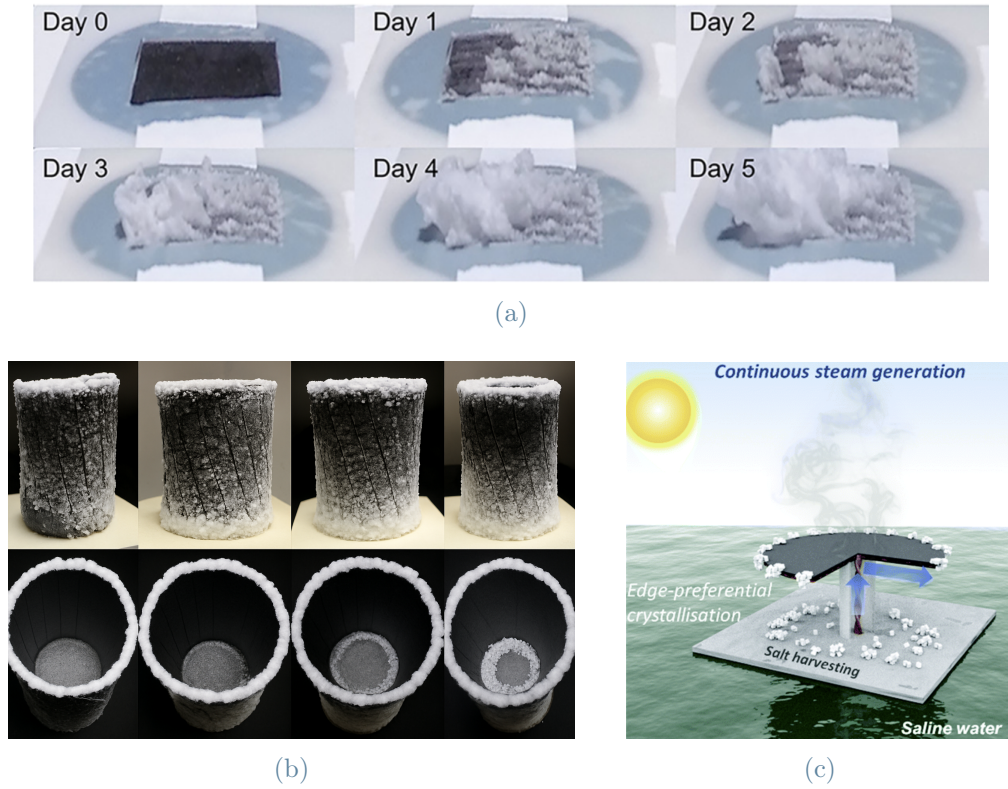


Figure 1.10: (a) Time-lapse of salt crystal formation on a GO leaf using a 15 wt% NaCl solution [9]. (b) Images of the 3D cup after 24 h of operation, treating brine with NaCl at 10, 15, 20, and 25 wt% from the first column up to the fourth one, respectively [10]. (c) Schematic illustration of the desalination process in the solar evaporators for continuous steam generation and salt harvesting [11].

Shielding effect against salt ions has shown to be a valid option with respect to mechanical removal and, according to its mechanism, it's classified into three categories, such as water-resistance through hydrophobic interactions, Janus configuration, and salt ion repulsion [8]. The first approach consists of enhancing the hydrophobicity of the solar absorber, and it was pursued by Zhao's group for the development of a water-repellent MXene membrane [56]. This novel solar steam generator was made from a $\text{d-Ti}_3\text{C}_2$ aqueous suspension mixed with a solution of fluoroalkylsilanes in order to reduce the surface energy of the final $\text{d-Ti}_3\text{C}_2$ film. While an unmodified hydrophilic membrane demonstrated signs of solar crystal formation after 24 h of desalination, the hydrophobic film showed only a few superficial changes that didn't affect the evaporation rate. The hydrophobicity of the second membrane didn't allow the flow of water and salt ions while permitting the passage of vapor through the pores of the membranes that in the hydrophilic film become clogged by salt deposition. Zhao et al. also reported a stable solar steam conversion efficiency of 71% over a period of 200 h under one sun of solar radiation

(equivalent to normal daylight intensity) with high salinity water, highlighting the potential of this salt-blocking technology for long-term desalination operations. Nevertheless, its intrinsic hydrophobicity allows only for a small volume of water to be treated, causing a lower evaporation rate with respect to the hydrophilic structure.

In this context, the Janus architecture with the upper and lower layers exhibiting distinct characteristics is recognized as a viable option. Indeed, the bilayer design allows the simultaneous integration of the salt blocking function of the hydrophobic structure with the enhanced evaporation peculiar to the hydrophilic structure [8]. The first research on Janus architectures with hydrophobic/hydrophilic properties began in the 90s with the work of Khayet and Matsuura et al. [57]. They realized flat-sheet structures by modifying, through phase inversion for casting solution, the surface of a hydrophilic base polymer, such as polyetherimide (PEI), with fluorinated macromolecules (SMM) of hydrophobic character. As a starting point, these designs showed optimal results, encouraging further research in the field of membrane distillation. In fact, many years later, scientists still develop innovative Janus structures, and among them, Yang et al. reported a nanoporous bilayered Janus membrane for efficient water evaporation distillation [12]. The design, illustrated in Figure 1.11a, consisted of a hydrophobic salt-blocking hierarchical layer of Cu_2SnSe_3 nanosphere array exhibiting a broad absorption band, and a hydrophilic filter membrane for water supply. Apart from avoiding salt precipitation, the upper layer also provided optimal photothermal conversion as well as numerous channels for vapor escape. Thanks to these features, the device was able to overcome both the salt accumulation problem of all-hydrophilic structures and the slow vaporization process of hydrophobic membranes. Notably, Zhao's group achieved a stable long-term water distillation process with a solar steam conversion efficiency of 86.6% under one sun. Similarly, Xu et al. achieved a flexible and salt-resistant Janus absorber with hydrophilic carbon black nanoparticles covering a layer of polymethylmethacrylate above a hydrophilic polyacrylonitrile substrate [58]. With this design, salts are blocked at the interface between the two layers and quickly dissolved due to the continuous water supply. However, the solar to thermal conversion efficiency was almost 50% under one sun of illumination intensity due to heat dissipation losses at the hydrophobic/hydrophilic interface. This problem was solved by adding an intermediate layer made of polymer foam and cotton wick that distributed seawater over all the evaporation area, and the final overall solar steam efficiency was 72%.

Besides tuning the hydrophobic property of the solar absorbers, scientists began to analyze the ion repulsion effect that some materials demonstrated towards salt recently. Ma et al. designed a novel asymmetric SWCNT/Gelatin (SGM) membrane with a hierarchical porous structure [59]. While the rough and porous upper layer facilitates light

absorption, the bottom dense and negatively charged thin surface exhibited size-sieving and Donnan effect against salt ions, inhibiting their diffusion while allowing water to flow through it easily. The SGM solar evaporator achieved a remarkable efficiency of 92% under one sun while maintaining excellent durability and reusability in high salinity environments. Meanwhile, Kashyap et al. developed a flexible anti-clogging film built from a porous polymeric matrix containing exfoliated graphite for enhanced light absorption and carbonized rayon to give homogeneity to the composite mixture [13]. The salt-blocking feature was achieved through careful pore size calibration and a coating of PEDOT-PSS on the surface. While PSS strongly bonds to the PEDOT thanks to its hydrophobic hydrocarbon branches, it leaves the hydrophilic sulphonic groups exposed to the solution, leading to weak adhesion with salt ions. After a period of exposure under one sun for more than 20 h, the group observed no changes in the pores of the structure but the appearance of a sediment due to the salt agglomerates formed in the pores that precipitated by gravity at the bottom of the container (Figure 1.11b). Furthermore, the performance of the devices was noted to be stable even with highly saturated salt water.

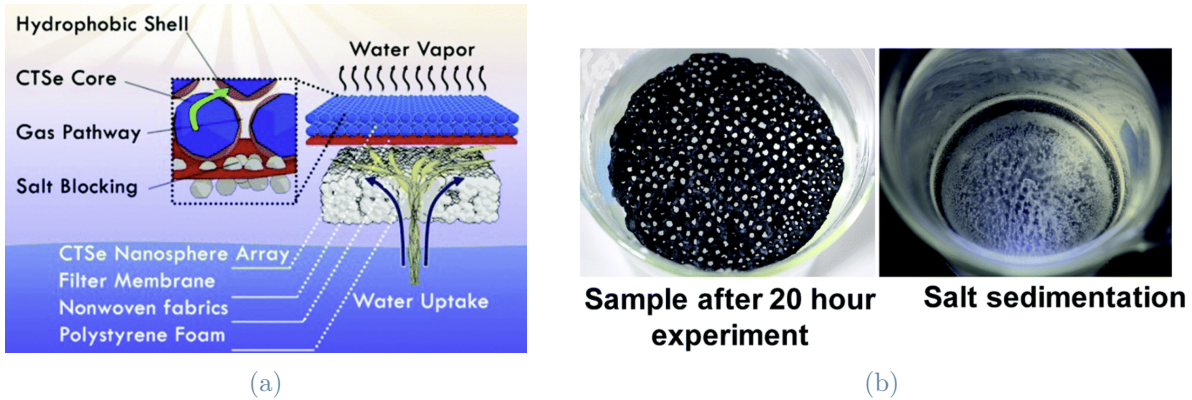


Figure 1.11: (a) Schematic illustration of the nanoporous hydrophilic/hydrophobic Janus membrane for solar water purification [12]. (b) Images taken after 20 h of operation. The membrane still exhibited open pores, while at the bottom of the container, a sediment was formed from all the salt particles that precipitated due to gravity [13].

Besides mechanical removal and shielding effect, force-driven fluid flow is the third approach to address the salt-clogging issue of solar water evaporators. Figure 1.8 categorizes this method into four categories according to three distinct mechanisms of action: concentration difference, gravity, and surface tension. Regarding the first working mode, it is implemented through two different strategies, such as natural dissolution and salt diffusion back into bulk water [8]. The premise of natural dissolution in dark to solve salt crystallization is that the evaporator rests during the night after continuous daytime

operation to allow salt accumulated at the evaporation interface to flow back and dissolve into the bulk seawater due to the concentration gradient between the two regions. Following this strategy, Xu et al. reported a thermally-localized solar still with a multistage design for optimizing the total mass and heat transport and enhancing the desalination performance [14]. The device is made of a thermal insulator behind the solar absorber to minimize heat losses, and an alternating series of capillary wicks and condensers separated by a small air gap. Evaporation of the brine occurs at the interface of each wick, where it is pumped from the container through capillary pressure. Then, steam passes through the air gap and dissipates energy by condensation. The real innovation behind this configuration lies in the capability to harness this released heat to drive the evaporation in the next stages, achieving vaporization enthalpy recycling. During a simulation of a day of total solar illumination, Xu's group observed a stable and high solar-to-vapor efficiency but also salt accumulation in the upper corners due to their salt diffusion resistance, a consequence of their longer distance from the brine reservoir (Figure 1.12a). Nevertheless, after turning off the light source, most of the salt diffused back into the bulk brine after 15 h, confirming the effective salt-rejection property of the evaporator. Despite reaching positive performances in many other research areas, desalination technologies based on natural dissolution in the dark still retain an important limitation, their financial burden on the overall cost for stopping the evaporation at night.

Fortunately, there's another approach to salt-rejection performances while exploiting the concentration gradient, too. Indeed, salt transport through diffusion mode is a strategy able to prevent salt accumulation by removing concentrated ions during the evaporation process [8]. From this perspective, many scientists considered some types of wood characterized by large interconnected holes in their structure for solving the salt clogging issue. An example is the salt-resistant balsa wood-based solar evaporators described in He et al.'s article [15]. Figure 1.12b shows how balsa wood was chosen thanks to its natural bimodal porous structure that exhibits both large and tiny vessels, while the evaporator exploits the interconnection between these channels to provide fast and efficient brine supply to the evaporation surface by means of capillary action. During operation, due to the large concentration difference between the almost saturated brine near the top layer of wood and the bulk seawater, convection and diffusion phenomena occur, causing salt ions to rapidly flow back to the bulk and dissolve, avoiding clogging in the channels. This process is possible due to the lateral brine diffusion through the pits, ray cells, and nanopores between the vessel channels, which ensures continuous and stable evaporation. He's group also noted that an additional salt placed on the surface of the evaporator was dissolved after 7 h of illumination under 2 suns. Overall, the experimental results showed a fast evaporation rate under 6 suns and excellent durability over time.

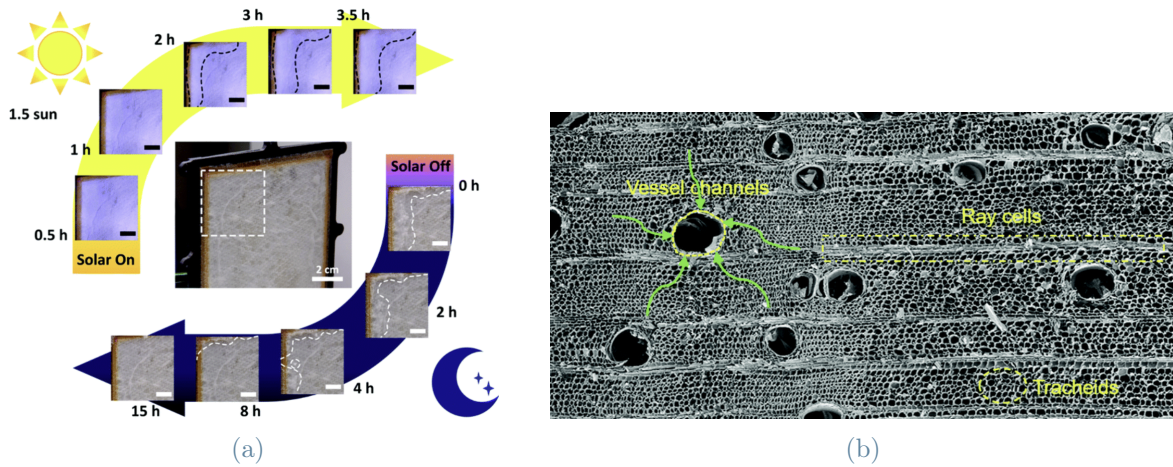


Figure 1.12: (a) Scheme of the salt-rejection performance encompassing a daytime salt accumulation period and a nighttime salt diffusion cycle. The approximated area covered by salt and its evolution in time is highlighted by white and black-dashed lines [14]. (b) SEM image of the porous structure of balsa wood showing wide vessel channels and horizontal ray cells surrounded by multiple narrow tracheids [15].

Other than wood, hydrogel-based solar evaporators were implemented for salt-free applications, too. Zhou et al. reported a hybrid hydrogel consisting of a hydrophilic framework of polyvinyl alcohol (PVA) with reduced graphene oxide (rGO) particles as additives that have the function of solar absorbers. The final structure exhibited a dense network of capillary pathways, which contributed to fast water replenishment to the evaporation surface with the help of the osmotic swelling effect. The long-term desalination performances arose from the presence of microscopic molecular sieves inside the hydrogel, while the concentration of residual salt in the evaporator was kept constant to a low level throughout the process due to the equilibrium established between the salt ion absorption and discharge into bulk water, as illustrated in Figure 1.13a [16].

Meanwhile, Zhang's research group developed low-cost carbon-based photothermal materials starting from recycled food wastes [17]. By means of carbonization treatment, these wastes achieve interesting properties for solar water evaporation, such as a porous structure and broadband light absorption, thus becoming the source of studies by scientists for potential future applications like water desalination. In particular, Zhang et al. reported an energy conversion efficiency under one sun of 84.1% with carbonized pasta, while other studies achieved values higher than 90% with enhanced water transport and controlled thermal insulation. Carbonized food wastes analyzed by Zhang possessed a highly porous structure with the unique property of being self-regenerating, which determined no salt clogging even during intensive long-term operations. In particular, the unique architec-

ture of carbonized lotus root (Figure 1.13b) presents rhizome holes that acted as perfect salt ion diffusion channels to avoid accumulation. Besides the optimal desalination performances, this study, as well as many others, represents a step forward for efficient and sustainable food waste recycling, turning them into carbonaceous photothermal materials for their deployment in applications with environmental benefits.

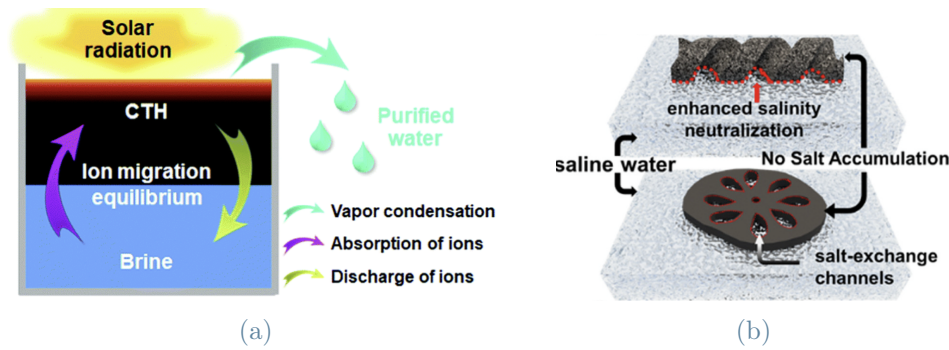


Figure 1.13: (a) Scheme of the hybrid hydrogels with capillarity facilitated water transport (CTH) showcasing the salt ion equilibrium [16]. (b) Simplified illustration of the self-regenerating porous structure of carbonized lotus root [17].

So far, it was discussed solar evaporators where the flow of salt ions was driven by the concentration gradient between the evaporation surface and the bulk seawater. An alternative approach to brine desalination is to carry away salt ions by a unidirectional fluid flow driven by gravity.

With this in mind, Liu et al. developed a hydrophilic polyaniline nanorod-coated photothermal fabric hanging between two tanks of seawater, unlike traditional evaporators that float above bulk water [18]. As depicted in Figure 1.14a, only the edges are continuously wetted by means of capillary action, thus soaking the rest of the fabric that is exposed to air. With this design, both the upper and lower surfaces can absorb solar radiation while the heat generated from the conversion is confined within the fabric with minimum losses towards air and the water reservoir. During evaporation, the high salinity brine is accumulated at the lowest point of the fabric, the center, where ultimately it is dropped down and collected in a container. The dropped brine was observed to be a source of heat loss, hence decreasing the evaporation rate of the fabric. However, Liu's group noted that by controlling the dropping speed in the range of 0.4 to 20 g per hour, the value didn't change. In particular, this result was also achieved by precisely regulating the hydrophilicity and capillary action of the fabric and the effect of gravity. After verifying that the generated vapor showed very low concentration of salt ions after condensation, the research group suggested the potential of other photothermal materials,

like carbon black and graphite, to be implemented in the hanging evaporation design. In recent years, a handful of researchers have been investigating the Marangoni effect for the instauration of a rapid fluid flow to remove salt ions. The phenomenon refers to forces generated as a consequence of the gradient in surface tension of a liquid surface. This will result in the appearance of a slip velocity that will cause the liquid to flow towards an area with higher surface energy. Morciano et al. conducted one of the first experiments that implemented the Marangoni effect for desalination application [19]. They realized a multistage solar distiller with multiple distillation stages separated by a small air gap to create a temperature gradient that drove the vapor flux coming from the hydrophilic evaporation layer towards the condenser, thus recycling the latent heat of condensation for the next stages (Figure 1.14b). While running experimental tests to simulate a typical daytime operation, Morciano's group correlated the absence of significant salt residues on the evaporation surface to the gradient in surface tension at the seawater-air interface determined by the difference in salt concentration. Since variations of the surface tension can also arise from temperature gradients, the group suggested that both factors act simultaneously to carry away salt ions.

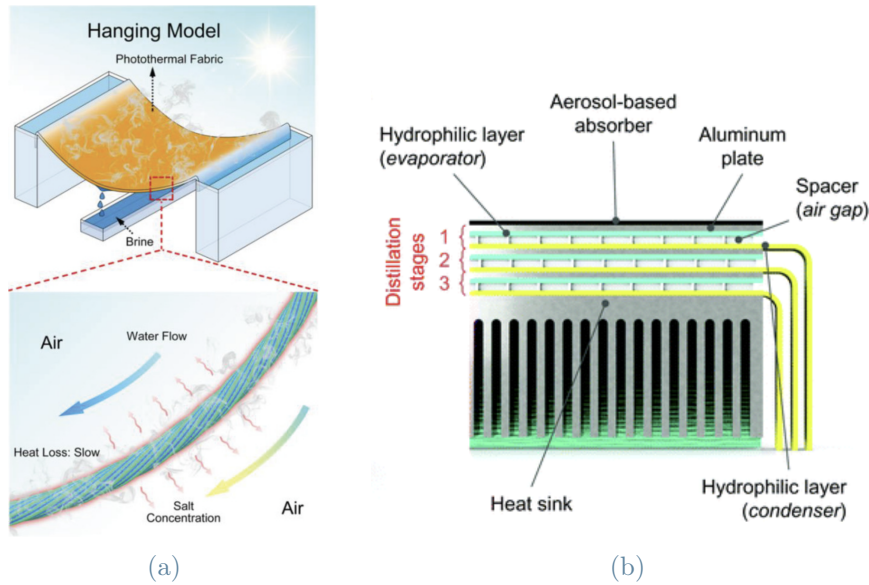


Figure 1.14: (a) Schematic illustration of the evaporation process in the novel hanging photothermal fabric [18]. (b) Detailed view of the components inside the multistage passive solar distiller. Seawater is taken from a tank and, by means of capillary action, is delivered to the hydrophilic evaporation layer while the distilled flux travels from the condenser and precipitates in a basin by gravity[19].

1.7.2. Microbial biofouling

The presence of numerous microorganisms and metabolic biomolecules in water represents a problem due to their accumulation on the surface of the evaporators. This phenomenon is called biofouling, and it carries the risk of hindering the normal performance of the devices by blocking the active sites for evaporation as well as inhibiting the efficient water supply through the channels. Moreover, the development of biofilm causes the contamination of drinking water, and it may be related to the emergence of serious illnesses. Even though no standardized method exists since few studies were focused on this problem, over the years, scientists have deployed many strategies to address the biofouling issue [46].

Wang et al. proposed an anti-fouling double-layered GO–chitosan/ZnO (GCZ) scaffold as a solar water evaporator [60]. The lower chitosan layer embedded with ZnO nanoparticles functioned as a unidirectional water pump, while the upper layer in graphene oxide aerogel served as the solar absorber. Wang's group observed the production of reactive oxygen species (ROS) at the surface of the bottom substrate due to the introduction of ZnO nanocrystals. These highly reactive molecules cause oxidative damages onto the bacterial cells, slowing them down from multiplying and growing. As a result, the formation of the biofilm was stopped, and the GO–chitosan/ZnO scaffold showed great solar steam conversion efficiency. During the comparison with a ZnO-free chitosan sample suffering from biofouling channel clogging, the GCZ exhibited great solar water evaporation efficiency over a period of 3 days.

Meanwhile, Yang's group focused on synthesizing anti-fouling copper-zinc-tin-selenide (CZTSe) nanocarambolas for deposition on a hydrophilic filter membrane (Figure 1.15a). In this way, the final device combined both the solar absorber and the vapor generator within a single structure. The CZTSe nanocarambolas were distributed uniformly on the upper part of the membrane, tightly intercrossed and bonded with each other, forming a nanoporous anti-fouling surface. Since the surface of these nanostructures is characterized by a hydrophobic layer, they can repel the uptake of water and salts, keeping the membrane dry and clean during the evaporation process. The device was able to indirectly heat water, minimizing the heat leakage that inevitably comes from direct warming of the liquid. After performing experiments like bending and airflow tests, scientists asserted an optimal mechanical stability for the membrane, further motivating its application in real-life solar water purification [20].

Another well-documented anti-biofouling approach consists of the implementation of non-biocompatible hydrophilic polymers to stop the formation of biofilms. As an example, Qiao et al. fabricated a monolithic 3D interfacial water evaporator made from the incor-

poration of bisphenol A (BPA) epoxy resins on polyacrylonitrile (PAN) foam [21]. They performed a controlled gas foaming technique to expand a 2D membrane into a monolithic structure by means of bubble nucleations. This process caused the appearance of numerous closed cells surrounded by nanofibrous walls that decreased the overall surface area, leaving less space for microorganisms to accumulate. Indeed, after leaving the BPA/PAN foam in natural water for two weeks, researchers detected a reduction in the bacterial population and the biofilm coverage on the surface by 1.4 and 2.7 fold compared to a neat PAN foam (Figure 1.15b). Qiao's group also measured high mechanical stability and water evaporation rates, highlighting the potential use of the gas foaming technique for foam-based solar evaporators in the future.

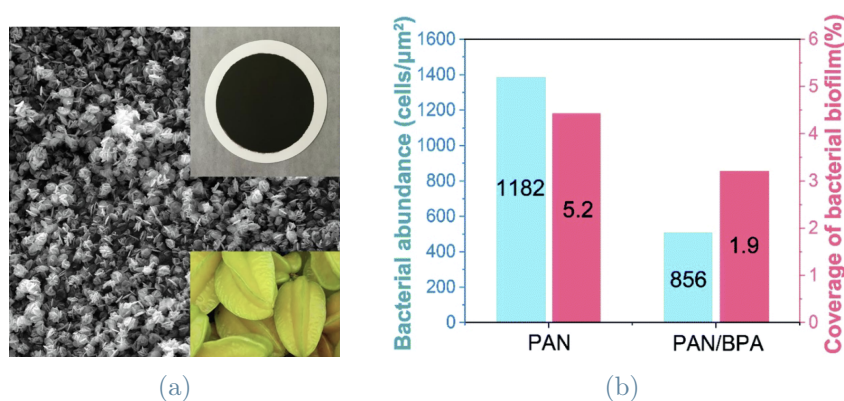


Figure 1.15: (a) SEM images showing the top view of the assembled membrane and CZTSe nanocarambolas [20]. (b) Comparison between the PAN and PAN/BPA (1:1) foams on their bacterial population and biofilm surface coverage after two weeks in natural water (pond) [21].

1.7.3. Volatile and semivolatile organic contaminants

The low rejection of volatile and semivolatile contaminants is a risk that may restrict the commercial availability of interfacial solar distillers. As in the case of microbial biofouling, the transfer of organic contaminants from bulk water to distilled water has been the focus of a few studies. In fact, many researchers have paid attention to the rejection of non-volatile compounds and achieved a removal rate close to 100%. In this context, chemicals like phenols represent a possible concern for the purity of condensed water due to their high volatilization and condensation rates. Shi et al. published one of the first studies on the VOC contamination in clear water from solar distillation [61]. In order to measure the concentrations of phenols in distilled water, they conducted chemical oxygen demand (COD) tests with a strong oxidizing species and measured the COD concentra-

tion in the water source and in the distillate. Shi's group recorded an increase in the COD concentration above 150% while testing original solutions with different phenol amounts, even reaching 378% with a concentration of 10 mg/L. The results not only proved the concentration of VOC in distilled condensed water but also their enrichment. Scientists suggested that the phenomenon can be attributed to the acceleration of VOC vaporization given by the phase change and mass transfer processes happening during water evaporation.

Chen et al.'s research was able to highlight the phenolic compounds as the chemical group with the highest risk to contaminate distilled water. One aspect of this study was the understanding of the correlation between Henry's constant, which governs the compound migration from the liquid to the air phase and vice versa, and the substance distillation concentration ratio, defined as the dimensionless ratio of the contaminants concentration collected in distilled water after condensation over its concentration in the source. The results showed that the concentration ratio is inversely proportional to the compound volatility. Considering this during an evaporation process, species that are more volatile than phenols, like anisole and aromatics with aniline group, are vaporized faster, and during mass recovery tests, no residues were found on the photothermal surface. The opposite occurred with compounds like benzoic acid that have lower volatility than phenolic species, since they were easily trapped on top of the evaporation zone. In terms of condensation, the process is slowed down when the temperature increases; however, compounds with a lower Henry's constant, so higher solubility in liquid, are more probable to condense in the distillate [22]. Chen's group also presented the opportunity to implement activated carbon in solar evaporation as a possible strategy for VOCs control. However, despite its good absorption performances in the early stages of the experiment, scientists reported an increase in the distillation concentration ratio after only 2h, as evidenced by the graph in Figure 1.16a. Therefore, without fast replacement or regeneration, activated carbon isn't a viable solution for contaminant removal on large-scale applications.

The concept of a super water-extracting gel (SWEG) made of highly hydratable alginate for handling VOCs and water purification was proposed by Zhang et al. in 2022 [23]. The overall internal structure of the solar evaporator consisted of a hypercrosslinked polymeric network where the water molecules can establish hydrogen bonds with the alginate polymer chains (Figure 1.16b). In terms of energy, these bonds are stronger than the dipole-dipole interaction formed between water and VOC molecules, hence the SWEG was able to collect water from the original solution at a molecular level, isolating the organic contaminants while delivering purified water to the evaporation surface. Scientists reported a VOCs removal rate of 99% for phenols via solar distillation under one sun, and eventual residues in the condensed water were deemed acceptable for the standard of

drinking water according to the World Health Organization. Nonetheless, the water evaporation rate was lower than some conventional technologies, encouraging further research for surpassing the trade-off between water yield and rejection rate [62].

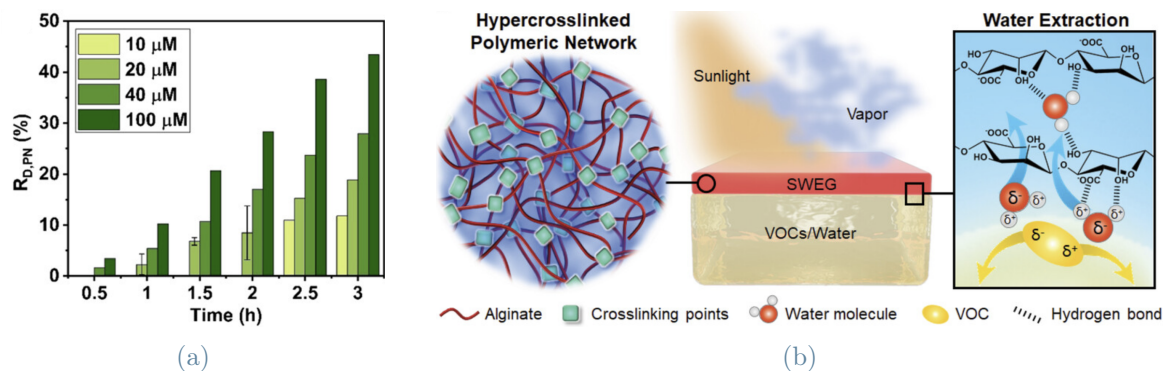


Figure 1.16: (a) Graph showing the phenol distillation concentration ratio of a solar evaporator using activated carbon for 3 hours with different initial content of phenols in the original solution [22]. (b) Set of images highlighting the internal hypercrosslinked network inside the SWEG layer and the hydrogen bonds between the polymeric chain of alginate and water molecules [23].

1.8. Photocatalyst integration in solar distillation

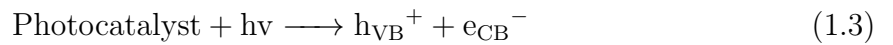
Many strategies have been proposed to solve the less documented issues of solar water evaporators, such as biofouling and low rejection of VOCs. Recently, many researchers have been developing multifunctional floating systems to take advantage of the photothermal effect in the presence of a photocatalyst working in synergy for efficient water distillation. The integration between these two technologies is possible due to the general alignment of the characteristics for manufacturing both photothermal absorbers and solar floating photocatalytic materials [46].

1.8.1. Mechanism of photocatalysis

The presence of a photocatalytic material confers on the evaporators a new and unique property, such as the continuous inactivation of bacteria and oxidation of organic contaminants by means of reactive oxygen species (ROS) generated from light-induced reactions. In a heterogeneous photocatalysis, where the catalyst is in a different phase with respect to the reactants, the overall process follows a five-step sequence [63]:

1. Mass transport of the pollutants or reactants from the liquid phase to the catalyst surface;
2. Adsorption of the pollutants on the catalyst surface;
3. Photocatalysis reaction in the adsorbed phase;
4. Desorption of the reaction products from the catalyst interface;
5. Mass transport of the byproducts into the liquid phase.

From the point of view of the kinetics of photocatalysis, the reaction rate is governed by the slowest step, which is usually identified in the mass transfer stage, or the reaction phase, due to the risk of recombination of electron-hole pairs. In a more detailed manner for the photocatalytic reactions, once the catalyst is irradiated by a UV-vis light source, it leads to the absorption of photons with energy ($h\nu$) higher than its band gap (E_g). As seen in the paragraph on semiconductor-based absorbers, this process leads to the transfer of an electron (e^-) from the valence band (VB) to the conduction band (CB), leaving behind a hole that can be modeled as a positive charge carrier (h^+). These light-induced electron-hole pairs tend to travel towards the surface before recombining, releasing free charge carriers capable of interacting with the adsorbed species. While the excited electrons react with oxygen to form superoxide radicals (O_2^-), the positive holes react with water molecules, generating hydroxyl radicals ($OH^\bullet$). These unstable species further react with the organic pollutants adsorbed on the catalyst surface and mineralize them into water and carbon dioxide. The overall photocatalytic reactions taking place can be summarized as follows:



It is clear now how the photocatalytic process enables fast oxidation of the organic contaminants by the photogenerated ROS on the surface; hence, the overall system is capable of removing pollutants and generating purified water [46, 63].

1.8.2. Superhydrophilic film formation on the photocatalyst

Among the numerous photocatalytic materials investigated over the past years, semiconductors are one of the most widely diffused classes, owing to their low cost and versatility. In this broad category, some oxides exhibit an interesting property: the remarkable capability to modify their surface hydrophilicity upon light irradiation.

The mechanism for this phenomenon was first suggested by Fujishima et al. in 1997 after observing a drop in the water contact angle from 72° to 0° on a TiO_2 film upon UV radiation [24]. This change was also found to be reversible after keeping the sample in a long period of storage in the dark (Figure 1.17a).

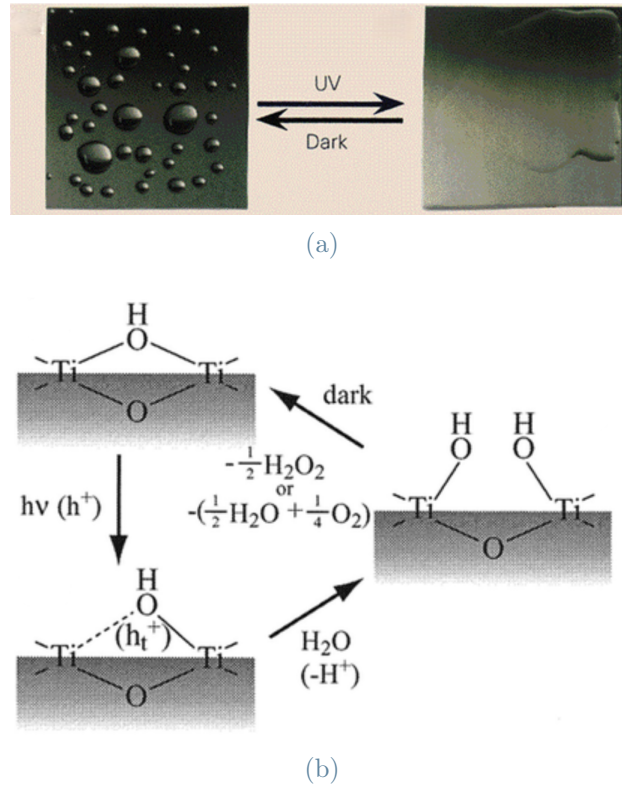


Figure 1.17: (a) The reversible wettability of TiO_2 films. After UV irradiation, a hydrophobic surface turned superhydrophilic in a short period of time [24]. (b) Reconstruction of surface hydroxyl groups. Initially, the hydroxyl group is bound to the oxygen vacancy. After irradiation, the photogenerated holes remain trapped by the lattice oxygen, weakening its binding energy with titanium. The resulting defect sites bonded with new hydroxyl groups that desorbed during long-term storage in the dark [24].

It was proposed that after photogeneration of free charge carriers and shuttling towards the surface, the holes from the valence band would oxidize the oxygen ions (O^{-2}), creating

multiple oxygen vacancies in the lattice. Meanwhile, the electrons reduce the titanium atoms from Ti^{+4} to Ti^{+3} , resulting in a more chemically active surface. The presence of these defect sites promotes the adsorption of hydroxyl groups from the environment to the surface, producing a dense layer with a very strong affinity with water. During conservation of the sample in the dark, the hydroxyl groups desorb, while Ti^{+3} oxidizes and the vacant sites get refilled with oxygen from air (Figure 1.17b). This work demonstrated how the photogeneration of the superhydrophilic layer doesn't initiate from surface contamination, but after structural and chemical variations in the topmost atomic layers, while the bulk of the catalyst remains unchanged. Additionally, like many other studies that replicated the experiment, Fujishima et al. reported the hydrophobic/superhydrophilic transition to occur around 30 minutes and the stability of the top layer for several days [64]. The presence of a superhydrophilic surface enhances water transport while inhibiting microbial adhesion and proliferation. Indeed, TiO_2 decomposes organic contaminants through photocatalysis, whereas the strong affinity with water allows liquid droplets to spread on the surface, further removing residual contaminants.

While TiO_2 is the most prominent example of a photocatalyst becoming superhydrophilic under UV irradiation, scientists have observed similar phenomena occurring in other semiconductor oxides, such as ZnO , WO_3 , and Fe_2O_3 . However, in these cases, the superhydrophilic layer usually exhibited lower performance or required high-maintenance working conditions.

1.8.3. Synergy in photocatalytic-photothermal absorbers

As anticipated in the previous section, one of the first advantages achieved after the introduction of a photocatalytic material with a solar absorber is the self-cleaning characteristic, able to remove microorganisms and VOCs from the evaporation surface, and so improving the lifetime of the system. This is a direct consequence of the superhydrophilic film formation on the catalyst surface, and many semiconductors can also act as partial water evaporators. This consequence arises from the photon-excitation recombination process that occurs when some electron-hole pairs don't reach the catalyst surface before recombining. As seen in paragraph 1.5.1, once these charge carriers recombine, they release energy in the form of light and heat. In the latter case, the result is a local heating of the lattice that can be exploited for vaporization on the evaporator surface [46]. Still, this side-effect is also considered one of the major factors in reducing the efficiency of the photocatalytic materials; hence, the design of the hybrid structure needs to account for the trade-off between the photocatalytic performance and the secondary water heating effect, according to the specific application.

Remarkably, in many studies, scientists discovered that the heat generated on the evaporator surface can improve the photocatalytic ability by acting on the mass transfer and reaction steps. Gan et al. proved this phenomenon while analyzing the enhanced photocatalytic effect of TiO_2 nanoparticles after the implementation of a sheet made of reduced graphene oxide (rGO). From previous studies, it was considered that the rGO sheet had only three main functions for improving the degradation of organic pollutants, such as blocking the photogenerated carriers from recombination while delivering them to the surface and augmenting light absorption and pollutants adsorptivity. This research demonstrated the additional contribution of the photothermal effect of rGO under NIR irradiation due to the surface plasmon resonance (Figure 1.18), very similar to the case of noble metal nanostructures described in section 1.5.2. The rise in the local temperature of the rGO system causes electrons to acquire more energy and move faster on the surface. As a result, the group reported an improvement of 38% in the photodegradation of a solution containing Methylene blue with respect to the neat TiO_2 nanoparticles [25].

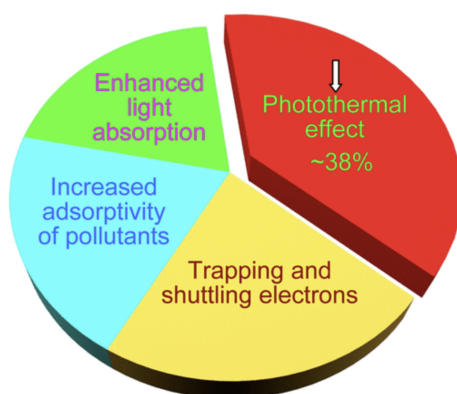


Figure 1.18: The four main factors introduced by rGO and contributing to the enhanced photodegradation activity[25].

Similarly, Li et al. reported an improvement in the photocatalytic performance of a carbon- TiO_2 yolk-shell heterostructure and linked it to the synergistic effect of photothermal effect and catalysis [65]. While the efficient heterojunction proved to be excellent in handling the transfer and separation of charge carriers, the photothermal excitation of the carbon core allowed an optimized injection of hot electrons into the TiO_2 shell. In addition, due to the favorable conductivity of the carbon spheres, the photogenerated heat is constantly delivered to the surface of the catalyst, subsequently increasing its temperature and accelerating the reactivity of oxygen species to organic pollutants. Thus, the photocatalytic degradation process is enhanced by the rise in the number of active sites on the catalyst surface.

Both of these recent studies are clear examples of how the research of this significant synergistic effect is frequently focused on TiO_2 nowadays. Indeed, among many semiconductors adopted for photocatalytic performances, titania has caught the attention of the scientific community due to its great photodegradation capability, as well as its chemical stability, high refractive index, and non-toxicity. In fact, thanks to these properties, TiO_2 proved to be efficient in antitumor, antibacterial, and antifouling applications. Furthermore, this thesis work is more oriented towards the development of a technological solution for the implementation of TiO_2 on a floating support combined with a photothermal material. Therefore, in the next sections, the properties and fabrication methods of TiO_2 will be discussed in detail.

1.9. Properties of nanotubular TiO_2

Among the various TiO_2 morphologies, nanotubes are the most appealing technological option. From the point of view of the electrical properties, this design offers new advantages such as high carrier mobility, quantum confinement effect, and outstanding photon-harvesting capability. Moreover, through specific production methods, it is possible to obtain vertically aligned nanotube arrays, which enhance the vectorial charge transport while lowering recombination effects at the trap sites that are present when electrons follow random transport pathways on particulate TiO_2 films [66]. The above-mentioned properties facilitate the photochemical and photocatalytic activity of the nanotubular structure. Meanwhile, considering the superhydrophilic layer formation on the surface of TiO_2 and the vertically aligned microstructure, water is easily driven by capillarity through the nanotubes from bulk water to the evaporation surface.

1.9.1. Thermal treatment of TiO_2 nanotubes

The as-prepared TiO_2 nanotubes result amorphous; nevertheless, they can be annealed to improve the crystallinity and reduce defects and internal stresses. With a high-temperature thermal treatment, phase transformation occurs, and titania can convert into rutile or anatase. From accurate X-ray diffraction patterns of annealed samples at different temperatures showcased in Figure 1.19, scientists found that anatase starts to appear from 280°C, and further increasing the heat would enhance its formation [26].

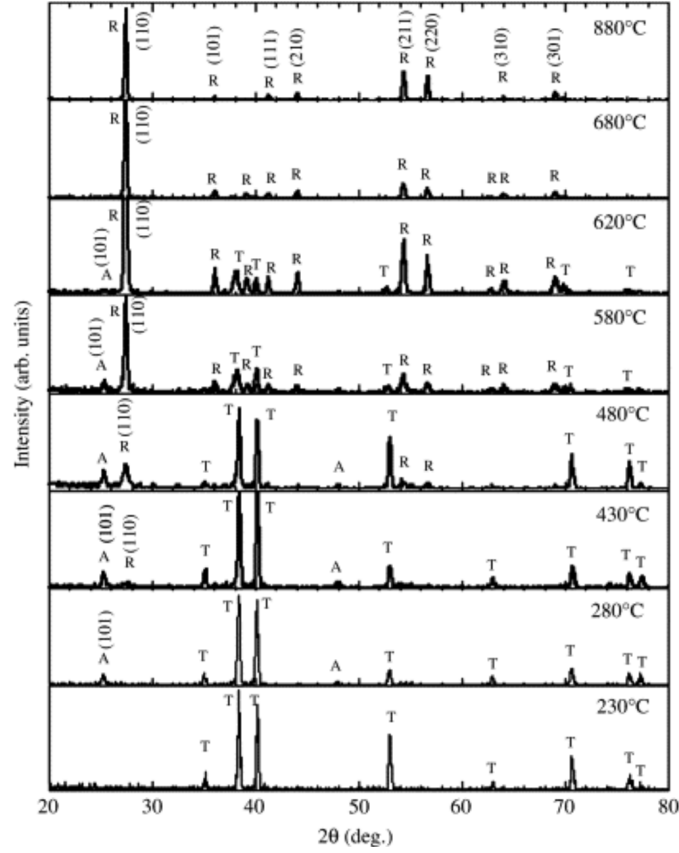


Figure 1.19: XRD patterns of titania nanotube array after annealing at different temperatures ranging from 230 to 880°C in a dry oxygen environment for 3h. The letters A, R, and T represent anatase, rutile, and titanium, respectively [26].

Rutile phase arises after 430°C and, with higher temperature, substitutes the anatase component up to 680°C. It was reported that after this value for extended annealing, TiO_2 nanotubes aren't stable anymore and start collapsing. After many experimental trials, the optimal annealing temperature was determined to be approximately 400°C. This decision was supported by multiple laboratory tests that highlighted anatase as the most favorable crystalline phase for surface wettability.

Although photo-induced superhydrophilicity occurs in all crystallographic forms of TiO_2 , there exists a correlation between the wettability and the crystalline structure of the titania nanotubes. During one experiment to evaluate the water contact angle of multiple nanotubular membranes after annealing and UV-irradiation, Yang et al. detected a value very close to 0° for the sample annealed at 400°C [67]. This experimental result can be explained by considering the crystal structure and surface morphology of the samples annealed at different temperatures. The wettability of the surface depends on the density of hydroxyl groups available for bonding with water molecules. This is inherently

related to the presence of superficial defective sites like dangling bonds, whose presence is very rich in amorphous TiO_2 . However, while the annealing temperature rises towards higher temperatures, these defects tend to lower their numbers in favor of a more organized crystallographic structure, leading to a steep increase in contact angle and loss of photoinduced hydrophilicity effect. At 400°C, when TiO_2 is almost entirely in anatase form, the structure is characterized by high surface energy and a modest concentration of oxygen vacancies that can increase under UV illumination. This phenomenon wasn't so dominant in the amorphous phase due to the abundance of defects; photoinduced hydrophilicity had only an auxiliary effect. With anatase TiO_2 , it became predominant and also generated more stable hydroxyl groups since the oxygen present in the vacancies works as their anchoring points. The crystal structure of rutile instead shows a weaker photo-induced hydrophilic effect and a lower density of surface defects, a consequence of its higher structural stability. At 800°C, due to the collapse of the nanotubes, the water contact angle registers its lowest value after UV irradiation.

Overall, anatase offers a better performance during photocatalysis when compared to rutile, which is also due to the lower recombination probability of charge carriers and a more negative conduction band that favors electron transfer to adsorbed species [68].

1.9.2. Synthesis of TiO_2 nanotubes by anodic oxidation

At present, there exist a variety of methods to synthesize TiO_2 nanomaterials, such as sol-gel techniques, micelle and inverse micelle methods, hydrothermal strategy, direct oxidation, chemical vapor deposition, and many more [69]. Among them, electrochemical anodization has been recognized as an efficient and simple approach to fabricate tubular and highly ordered nanotube arrays with controllable morphologies [66]. The fundamental mechanism of the process is the oxide growth on a pure titanium substrate immersed in an electrochemical cell where it works as the anode. Anodization can be conducted in three different strategies:

- Galvanostatic mode, in which a constant current is imposed, flowing between an anode and a cathode.
- Potentiodynamic mode, where there's a constant potential difference between the two electrodes.
- Potentiostatic mode, by varying the potential with time.

In all three of these approaches, the morphology, as well as the length of the nanotubes, can be tuned by modifying both the electrical and chemical parameters of the experimental setup. In one of the first research studies on titanium anodization, Zwilling et al. were able

to electrochemically grow porous TiO_2 nanotube arrays via potentiostatic anodization of a titanium sample immersed in a solution with chromic acid and hydrofluoric acid [27]. Despite achieving a final layer with evident inhomogeneities, this work demonstrated how the presence of fluoride ions in the electrolyte could favor the growth of a self-organized nanotubular structure (Figure 1.20).

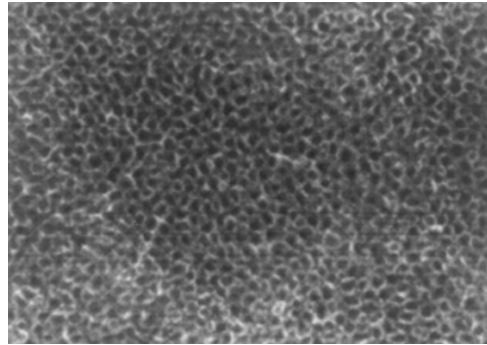


Figure 1.20: High-resolution scanning electron micrographs of anodic oxide film grown on a titanium substrate in CA/HF solution [27].

The above mentioned defects found on the nanotubes were sidewall irregularities appearing as ripples of varying thickness of the wall (Figure 1.21a). Their presence was associated with current fluctuations during anodization that cause instabilities in the ion concentration in the electrolyte. Macak et al. were able to suppress this negative effect by adopting an organic-based and highly viscous electrolyte instead of an aqueous one, and the results coming from SEM measurements confirmed smooth and regular nanotube arrays (Figure 1.21b and 1.21c). Aqueous electrolytes were fundamental in analyzing the direct proportionality between the pore size of the nanotubes and the applied potential. However, they were limited by the short tube length due to the very acidic environment as a consequence of fluoride ions. Since the morphology of the nanostructures is related to the equilibrium between the electrochemical oxidation of the metal surface and the chemical dissolution of the oxide layer, an excessive amount of those ions would favor the latter process, shortening the nanotube length even after long exposure time and higher applied voltage. One solution was tailoring the pH of the electrolyte by switching from a strong acidic reagent like hydrofluoric acid to a less aggressive fluoride ion source such as ammonium fluoride. Macak et al. preferred another approach, the inhibition of the ion diffusion coefficients in the electrolyte by using a glycerol-based solution. Since diffusion is the main actor in regulating chemical dissolution, inside a highly viscous electrolyte, ions move less freely and are confined mainly at the pore tip [28]. The group reported a growth of the nanotubes up to $7\text{ }\mu\text{m}$, while in another research where ethylene glycol was

used instead, scientists were able to achieve nanotube growth as a hexagonal close-packed pore array with the highest length recorded at $261\text{ }\mu\text{m}$, illustrated in Figure 1.21d.

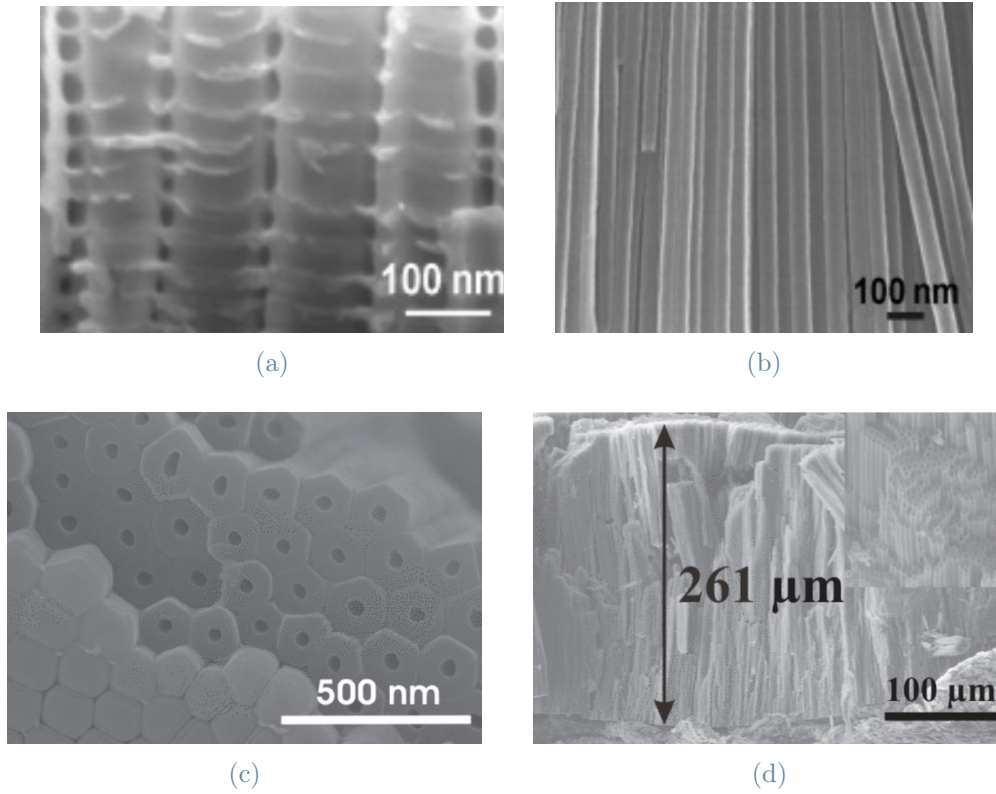


Figure 1.21: (a) SEM images of conventional anodic TiO_2 nanotubes with marked inhomogeneities and (b) smooth TiO_2 nanotubes $7\text{ }\mu\text{m}$ long produced in glycerol electrolyte with 0.5 wt% NH_4F [28]. (c) A bottom-view SEM picture from a TiO_2 nanotube layer formed in ethylene glycol at 60 V and HF concentration of 0.05 M and (d) a cross-section SEM image of the TiO_2 nanotubular layer formed after 15 h anodization at 120 V at a HF concentration of 0.2 M [29].

The main limitation of organic electrolytes originates from the lower diffusion coefficients compared to aqueous electrolytes. Basically, the transport of oxygen ions is mitigated in a very viscous solution, and therefore, the process of oxidation is impeded. Over the years, scientists have found that a small amount of water, not higher than 5 wt%, can reduce the viscosity of the electrolyte while still limiting the chemical dissolution and work as a source of oxygen and hydroxyl ions [66].

1.9.3. Growth stages of TiO_2 nanotubes

Anodization to form a nanotubular oxide on a titanium substrate is generally conducted in an electrochemical cell with a suitable electrolyte where the metal sample works as the anode, and it's placed in front of the counter-electrode, which serves as the cathode for the process. With this configuration setup only the front surface of the titanium oxidizes, leaving the back of the sample untreated. Figure 1.22 also depicts another interesting experimental setup where the counter electrode surrounds the anode, and consequently the final oxide layer will cover its entire surface [30].

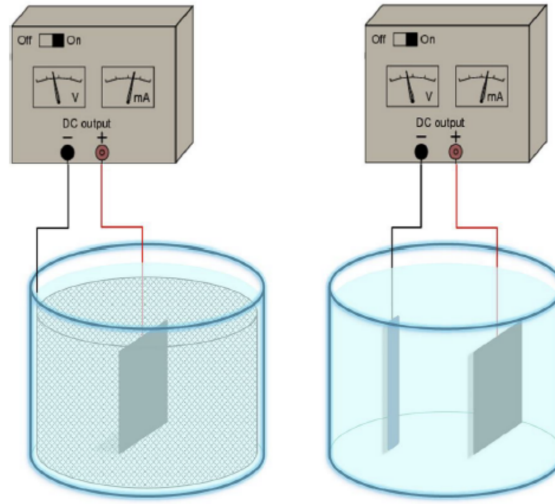


Figure 1.22: Experimental setup for titanium anodic oxidation. On the right, the counter electrode surrounds all the surface of the anode, while on the left, only the front face [30].

Once a potential difference is established between the two electrodes and current starts flowing in the cell, the electrochemical process starts. At the anode surface, titanium oxidizes, releasing electrons and Ti^{4+} ions, which interact in the electrolyte with hydroxyl ions produced from the dissociation of water molecules. From this reaction, hydrated titanium oxides are formed, but under the strong electric field, it follows a dehydration process that causes these species to dissociate into titanium oxide and water. At the same time, some titanium and oxygen ions interact with each other, further promoting the formation of solid metal oxide particles.





At the cathode, protons are reduced, and hydrogen is formed:

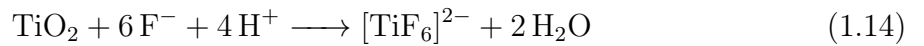


After initiation, the electric field drives the ion migration through the oxide layer to continue its growth at the metal-oxide interface. While the new layer grows in thickness d under constant applied voltage U , the field strength $F = U/d$ decreases over time, and so does the ion migration as well. The result is an exponential decrease in the current flowing in the cell until the field effect is reduced to a value that it can't promote ion transport any longer. Below is reported the high field law expressing the relationship between the current I and the electric field:

$$I = A \exp(BE) = A \exp\left(\frac{BU}{d}\right) \quad (1.13)$$

At the point where the current remains low over time, a finite oxide thickness is achieved that mainly depends on the anodization voltage [31, 70].

However, the presence of fluoride ions inside the electrolyte strongly affects the reaction process with the formation of fluoride complexes with titanium that are water-soluble. Two reactions can be identified for the promotion of these complexes, namely chemical dissolution of the oxide layer and complexation of the Ti^{4+} cations that are ejected at the oxide-electrolyte interface after traveling through the oxide driven by the applied voltage:



Now, with the presence of fluoride complexes, the competition between oxide formation and chemical dissolution arises, leading to a different behavior of the current-time characteristic curve, which can be identified as three different cases reported in Figure 1.23 depending on the concentration of fluoride ions in the electrolyte.

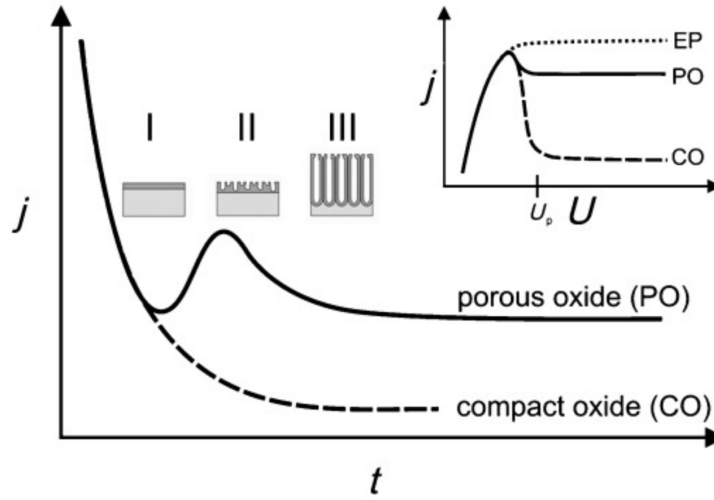


Figure 1.23: Typical current density–time (j – t) characteristics after a voltage step in the absence and presence of fluoride ions in the electrolyte. Either compact oxide CO (fluoride-free) or porous/tubular metal oxide formation PO (containing fluoride) forms by different morphological stages (I–III) [31].

For very low fluoride content (≤ 0.05 wt%), the curve doesn't differ from the fluoride-free case, and the anodized sample shows a compact oxide film (CO) of finite thickness after a certain period of time has passed. In the opposite case, if the fluoride concentration is very high (ca. 1 wt%), no oxide formation is observed since all the titanium ions react with the excessive fluoride anions to form soluble complexes, causing electropolishing of the surface to occur [31].

When the electrolyte contains an intermediate quantity of fluoride ions, as a result of both oxide formation and Ti^{4+} solvatization, a porous or nanotubular metal oxide structure will form following three different morphological stages. In the first stage, the current decreases as mentioned before due to coverage of its surface by a thin and compact oxide layer. During stage II, nanoscopic etch channels partially penetrate the compact oxide, forming an initial porous layer, causing a rise in the current as the surface area of the electrode increases. Up to this point, the pore formation is random since the chemical dissolution is non-uniform; however, under optimized conditions beneath the first porous layer, self-ordering of the pores is established, and current reaches a constant value in phase III. Steady-state conditions between oxidation and dissolution are achieved, and stable pore growth is initiated. The transition from a hexagonal nanoporous to a nanotubular structure is due to the formation of a fluoride-rich layer at the metal-oxide interface, as shown in Figure 1.24. Fluoride ions travel through the porous oxide towards the metal faster than O^{2-} ions thanks to their smaller ion size, leading to their accumulation at the cell boundaries. These regions with titanium fluorides are more prone

to chemical dissolution under water, which easily dissolves this layer between the cell and creates distinct tubular shapes [70].

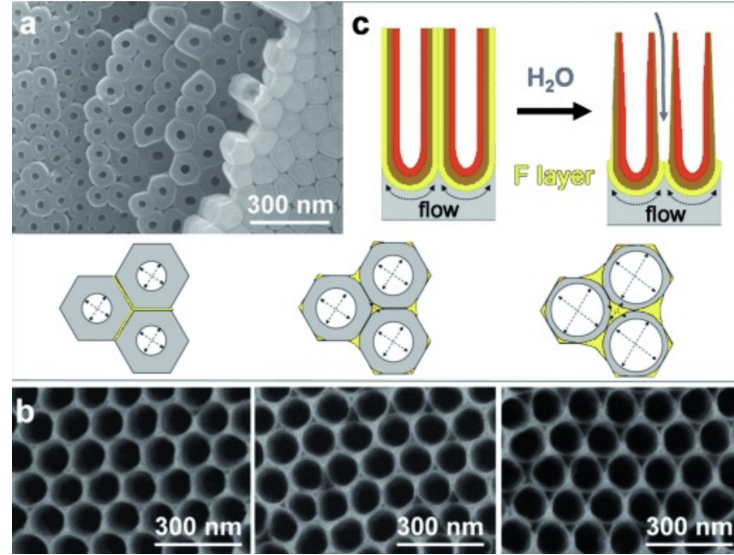


Figure 1.24: (a) Formation of tubes from porous structures, illustrated by an SEM bottom view of a nanotube layer cracked off from the metal substrate at a slight angle. The bottom of a tube layer consists entirely of a close-packed hexagonal pore layer that is gradually converted into round tubes. (b) Transition from a porous to a tubular structure (left to right). (c) Representation of the formation of a tubular morphology from an originally porous morphology by selective dissolution of fluoride-rich layers and preferential etching at triple points by H_2O in the electrolyte [31].

1.9.4. Limitations of TiO_2 nanotube arrays

One major drawback for the implementation of TiO_2 in photocatalytic performances is its intrinsic wide bandgap energy. With 3.2 eV, only photons with wavelength in the UV regions can be absorbed for photogeneration of carriers; however, they comprise only 7% of the entire solar spectrum. Numerous approaches like metal and non-metal doping or composite semiconductors have been tested for lowering the bandgap and so improving light absorption in the visible range [66].

Noble metal doping in the form of nanoparticles is an optimal solution since the surface plasmon resonance is excited with visible light, and their dispersion constitutes an additional energy level that lowers the bandgap energy of the TiO_2 matrix. Additionally, they can act as electron trap sites to delay photogenerated charge recombination and extend their lifetime. Yoong et al. reported a reduction to 2.4 eV from doping with 10 wt% Cu loading through a wet precipitation method [71].

Recently, scientists have documented extensively doping with transition and rare earth metal ions. Their introduction in the TiO_2 lattice causes the appearance of impurity energy levels in the bandgap, less negative than the conduction band, while others are less positive than the valence band edges of titanium oxide. The electron transfer between the oxide and the metal ions retards any recombination events. By doping in a solution with hydrofluoric acid and iron nitrate, Sun et al. achieved Fe^{3+} -doped TiO_2 nanotube arrays exhibiting a shift towards higher wavelengths of the absorption spectrum [32, 66]. Sun et al. also evaluated the degradation rate of an aqueous solution containing Methylene blue (MB) with three different doping levels of Fe^{3+} ions (Figure 1.25).

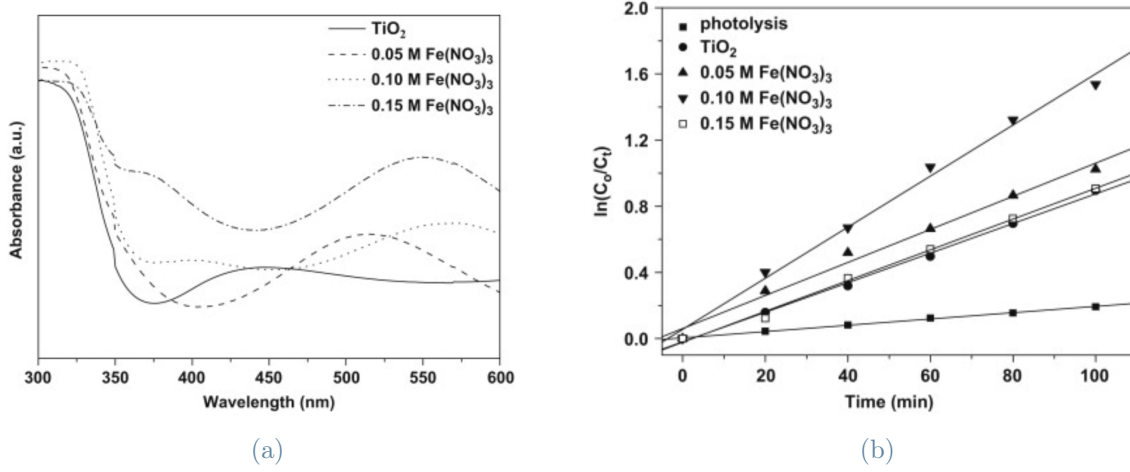


Figure 1.25: (a) UV-vis spectra of the TiO_2 nanotube array film and Fe^{3+} - TiO_2 nanotube array films. (b) Comparison of photocatalytic degradation rate of MB for the undoped TiO_2 nanotube array film and three different Fe^{3+} - TiO_2 nanotube array films. C_0 and C_t are the initial and reaction concentrations of the MB aqueous solution, respectively [32].

In order to further suppress the recombination of the photogenerated electron-hole pairs, non-metal ion doping has proved to be an efficient strategy. While analyzing the substitutional doping of C , N and S instead of oxygen in anatase TiO_2 , scientists reported a narrowing of the bandgap at 2.47 eV due to the formation of localized electronic states above the maximum of the valence band of pure TiO_2 , enabling visible-light harvesting [66]. This photocatalytic property was assessed through X-ray photoelectron spectroscopy [72], while photoluminescence measurements, reported on Figure 1.26a, showed intensity peaks decreasing while shifting at higher wavenumbers with non-metal doping, highlighting the lower frequency of recombination phenomena [33].

Another approach for visible-light harvesting is the engineering of a composite semicon-

ductor by coupling TiO_2 with a narrow bandgap semiconductor. Delivering the electrons from the narrow gap to the larger ones enables achieving wide charge separation and limiting recombination effects (Figure 1.26b). A wide range of semiconductors, including CdS , $CdTe$, $CdSe$, ZnS , ZnO , ZrO_2 , $GaAs$ and GaP , have been integrated into TiO_2 . As an example, sensitization of TiO_2 with CdS for the realization of nanocomposites can extend the absorption spectrum in the visible region, and both materials can be excited with photons of higher wavelength, and the more efficient charge separation aids the photocatalytic property. Indeed, it was observed that the degradation rate of organic impurities in aqueous suspension improved while increasing the CdS content [66].

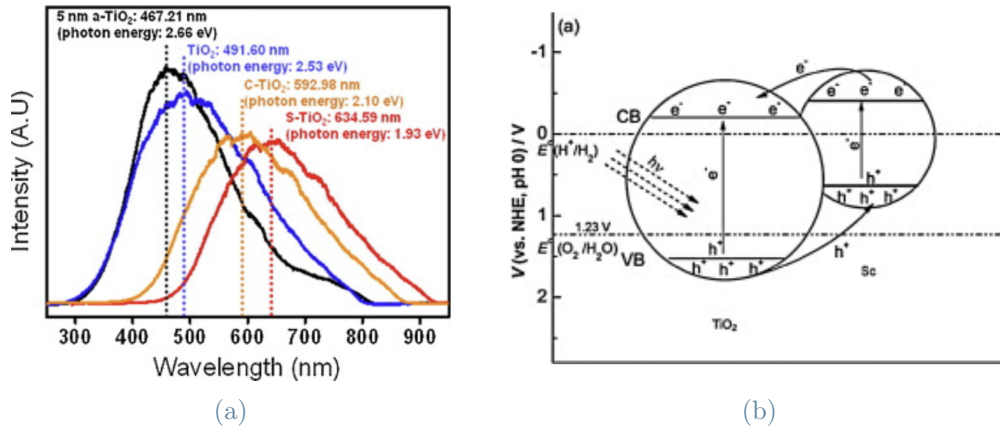


Figure 1.26: (a) Photoluminescence spectra of commercial anatase TiO_2 , laboratory grown TiO_2 , C-doped TiO_2 and S-doped TiO_2 photocatalysts [33]. (b) The band structure of composite TiO_2 photocatalysts and the migration of photogenerated carriers. In this image, electrons are injected from the other semiconductor to TiO_2 while holes simultaneously transfer from TiO_2 to the semiconductor [34].

Another important aspect to consider when dealing with anodic oxidation of Ti is the high surface roughness exhibited by the final nanotube arrays with small ripples present on the sidewalls. From the images in Figure 1.27 achieved through Field Emission Scanning Electron Microscopy (FESEM), it was observed that the area density of hexagonal nanotube arrays was much lower than expected, localized only in small regions [35].

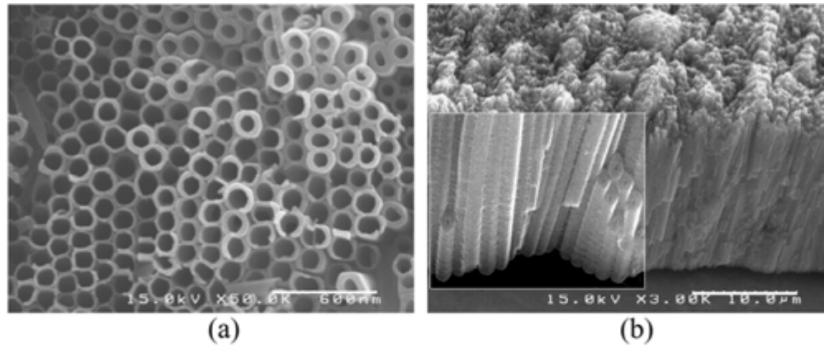


Figure 1.27: (a) A top view FESEM image of a TiO_2 nanotube array formed by the first step of the anodic oxidation process at 50 V in an ethylene glycol electrolyte containing 0,25 wt% NH_4F and (b) a cross-sectional view image [35].

Together with a careful management of the chemical and electrical parameters, scientists suggested a multi-step anodization process to exploit the hexagonally shaped imprints left on the Ti substrate after removing the nanotube array formed during the first anodization step. These geometrical dimples serve as a template for the second array guiding the growth of highly ordered self-organized hexagonal TiO_2 nanotubes as depicted in Figure 1.28. Han et al. performed a three-step anodic oxidation process where the first two layers were peeled off ultrasonically from the substrate. This research confirmed an increase in the area density of hexagonal TiO_2 nanotube arrays with respect to the first anodization step, whose time span has been observed to proportionally affect the concentration of the dimples left after ultrasonication [35].

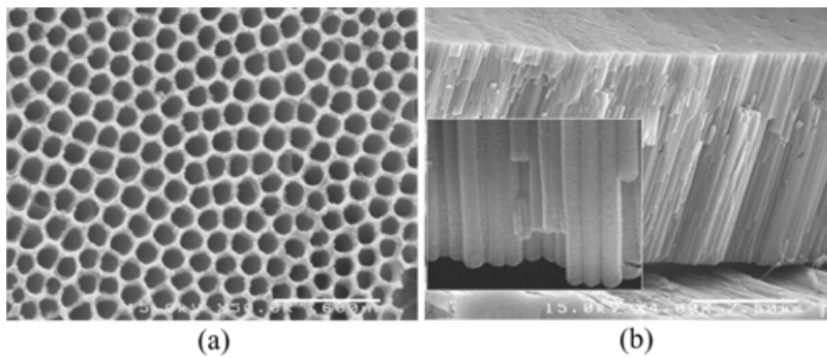


Figure 1.28: (a) A top view FESEM image of a TiO_2 nanotube array formed by the second anodization of the multi-step anodic oxidation process at 50 V in an ethylene glycol electrolyte containing 0,25 wt% NH_4F and (b) a cross-sectional view image[35].

1.9.5. Free-standing TiO_2 nanotubular membranes

Thus far, it was discussed how to fabricate highly ordered TiO_2 nanotube arrays attached to a Ti substrate. However, the presence of a compact, metallic substrate can lead to unwanted issues that can hinder the final properties and applications of the overall structure due to the mismatch between the characteristics of the two materials. Therefore, the ultimate goal should be a free-standing nanotubular membrane separated from the substrate and without closed bottoms. While many approaches have emerged over the years, the main challenge is handling the membrane detachment without causing its rupture, especially when dealing with thinner films with large area [31, 73]. The typical methods for membrane separation can be classified into four main categories:

- Mechanical delamination, in this category, the membranes are detached by mechanical splitting through solvent evaporation or ultrasonic vibration. These are safe and simple methods; however, the obtained film needs further treatments to open the closed bottoms.
- Physical parameter regulation, such as voltage, temperature, and electrolyte composition. By controlling the voltage, scientists can tailor the local acidification at the bottom of the nanotubes, enhancing its fragility. A thermal treatment can assist the separation of the membrane via the exploitation of different mechanical stability and etching selectivity between the upper and lower nanotube layers. This is particularly helpful during a third step anodization process where amorphous TiO_2 is growing over anatase TiO_2 nanotubes. Regarding the electrolyte composition, with the addition of substances like sodium molybdate, a different etching contrast was achieved between the oxide and the substrate.
- Chemical separation, consisting of chemical dissolution of the substrate or chemically assisted detachment. In particular, the latter process should be the final step of the above-mentioned temperature-assisted membrane detachment, both of them illustrated in Figure 1.29, where the lower amorphous nanotubular layer is easily dissolved by an aggressive reagent like oxalic acid or hydrogen chloride.
- Selective dissolution, a newer technique where flow-through membranes are achieved by selectively removing the bottom layer of the nanotube arrays with inductively coupled plasma (ICP) etching.

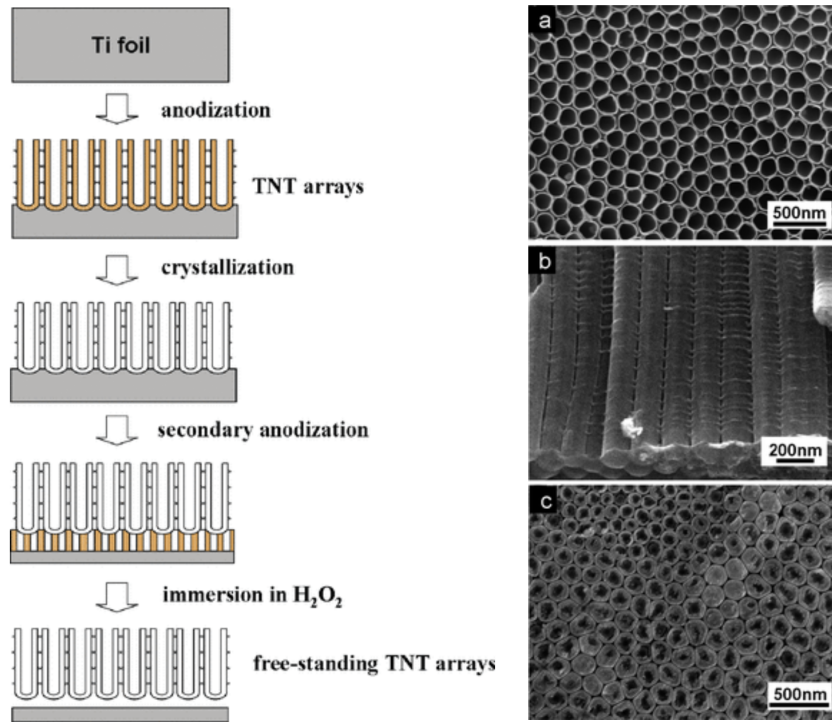


Figure 1.29: Schematic illustration of the procedure for preparing free-standing crystallized TNT arrays anodized in ethylene glycol with SEM images of (a) top view, (b) cross-sectional view, and (c) bottom view [36].

1.10. COPE project

This thesis work was conducted according to the guidelines from the COPE research project, funded in 2022 by PRIN PNRR, with the aim to develop efficient interfacial solar evaporator for long-term water production without organic contaminants. All the limitations mentioned in the previous paragraphs hinder the lifetime of this new technology and, consequently, its large-scale application. Therefore, by proposing an innovative configuration of a solar evaporator, this project hopes to stimulate further technological progress and research. The suggested prototype combines three distinct elements schematized in Figure 1.30:

- A TiO_2 nanotubular membrane, exhibiting self-cleaning and photocatalytic properties and serving as a support for the photoabsorber.
- Semiconductor nanoparticles, acting as the photoabsorber.
- A wooden floating support for the active elements, and also to supply water to the membrane while ensuring thermal insulation.

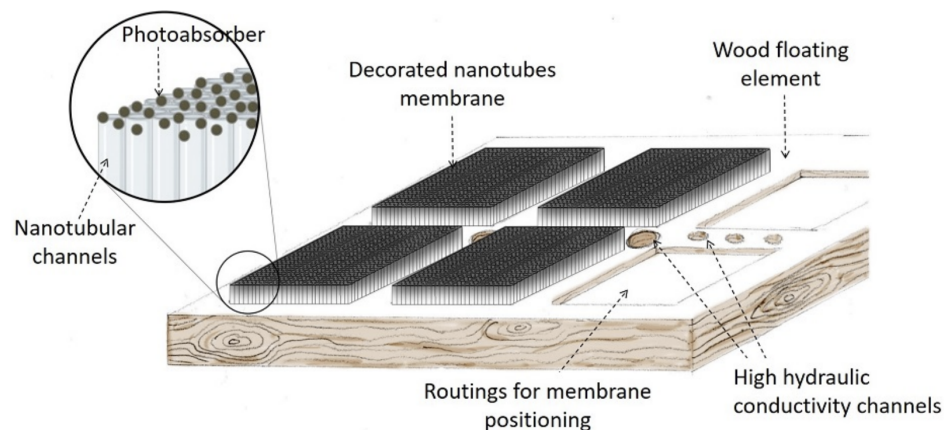


Figure 1.30: Schematic illustration of the assembled active elements for the photothermal evaporator envisaged in the COPE project.

The production of the TiO_2 nanotubular membrane is in charge of the Politecnico di Milano unit due to its strong expertise in the anodic oxidation of metallic samples, and it will also select the best parameters for the oxide growth to obtain the best performances in terms of photocatalytic activity and wettability. Both a preliminary characterization of the morphology as well as one regarding the photodegradation of organic dyes will be conducted in collaboration with the Università degli Studi di Milano unit, which also oversees the optimization of the floating support.

Meanwhile, the Università di Trieste unit is responsible for the synthesis of semiconductor core-shell nanoparticles directly on the TiO_2 nanotubes or after their growth with suitable anchoring molecules. In particular, two populations of nanoparticles will be produced; the first one will enhance the photothermal conversion, while the other will improve the photocatalytic activity. Through characterization tests, the perfect mix between these two populations will be tailored, assuring an optimal compromise of the two effects.

In the next chapter, the experimental approach and methods followed for the production of free-standing TiO_2 nanotubular membranes, as well as the tests performed following the photo-degradation of a solution containing Rhodamine-B to evaluate the photocatalytic property of the film before and after photoabsorber nanoparticles loading, will be discussed.

2 | Materials and methods

This project began with a detailed examination of all the steps included in the experimental procedure for engineering free-standing TiO_2 nanotubular membranes, starting from the choice of the chemical and electrical parameters. The performance of the membranes in terms of photo-degradation of organic components was assessed through photocatalytic characterization tests performed both on free-standing films and on layers still anchored to the Ti substrate. In the last part of this research, quantum dot loading was performed, and its influence was confirmed while conducting new photo-catalysis tests that followed the same procedure. More details covering all the experiments conducted in this project will be described in this section, whose structure replicates the time scale of the project:

1. Discussion on the fabrication of free-standing TiO_2 nanotubular membranes, covering the chemical reagents, materials, and laboratory equipment involved;
2. Description of the experimental approach followed for conducting photocatalytic characterization tests;
3. Description of the experimental procedure for achieving quantum dot loading on free-standing membranes.

2.1. Free-standing TiO_2 nanotubular membranes

2.1.1. Preparation of the Ti substrate

The preparation of the Ti substrate where the nanotubular oxide grows starts by cutting a 1.5 cm X 1.5 cm square sample with a thickness of 0.5 mm from Alfa Aesar grade 2-Titanium sheets. The majority of the tests were performed with Ti squares of these dimensions, while in some cases the experiments started with 2 cm X 2 cm or 2.5 cm X 2.5 cm squares instead. An acceptable sample after being cut should present no scratches on its surface and be perfectly flat with no curves or residues in the cut area. Subsequently, the component was immersed in a solution with ethanol and placed inside a sonication machine for 10 minutes to remove any dirt or powder residues on its surface. The cleaning

process was repeated with the sample soaked in distilled water and then dried using compressed air.

2.1.2. Chemical reagents and electrolyte preparation

Regarding the anodic oxidation for membranes production, the formulation of the standard electrolyte consisted of an ethylene glycol-based solution with three other components whose concentrations are reported below:

- 0.1 M ammonium fluoride (NH_4F).
- 2 M distilled water (H_2O).
- 1.5 M lactic acid ($C_3H_6O_3$).

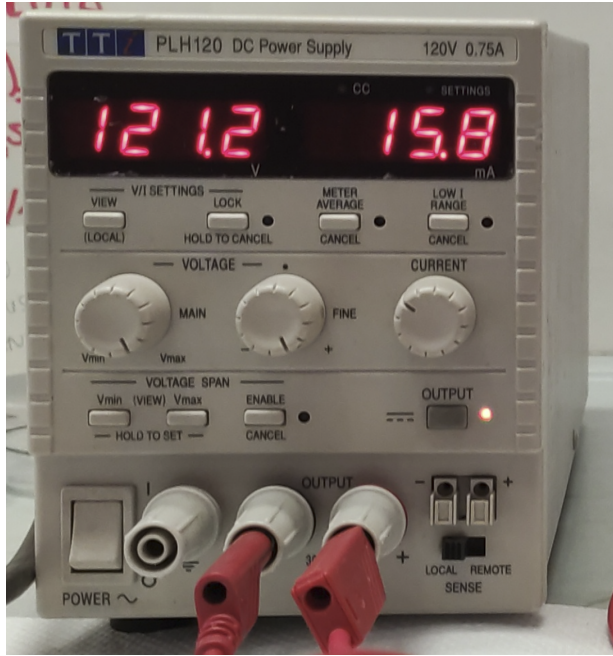
First, the NH_4F in the form of powder was weighed in a plate on a scale, then dropped into a beaker with enough space for stirring the final solution without the risk of spilling. Then, the desired volume of distilled water, lactic acid, and ethylene glycol was achieved with a measuring cylinder and poured into the beaker with ammonium fluoride. In order to homogenize the electrolyte and allow the reagents to mix and dissolve the solid part, the mixture was stirred with the help of a magnetic stirrer for 20 minutes at 700 rpm. While the reasons behind the addition of ammonium fluoride and a small quantity of water were covered in paragraph 1.9.2, the inclusion of weak organic acids was analyzed in previous research works, where a field supporting effect capable of enhancing the properties of the electrolyte was observed. In particular, the voltage for dielectric breakdown was extended towards higher values, enabling the growth of longer and more robust TiO_2 nanotubes. For the detachment from the substrate, a solution with 1 M hydrochloric acid (HCl) was used.

2.1.3. Electrochemical cell configuration

The synthesis of TiO_2 nanotubes was achieved through electrochemical oxidation where the Ti samples were anodized following two distinct anodizing conditions:

- Galvanostatic conditions, where the current density between the two electrodes is kept constant while the voltage evolves in response to the oxide formation and reaches a constant value when nanotubes start to form. Figure 2.1a illustrates the power supply exploited for this condition.
- Potentiodynamic conditions, in which the difference in potential varies in time, in this case, a ramp with slope 2 V s^{-1} was employed, and upon reaching the anodiza-

tion voltage, it is kept constant while the current response varies in time. This condition was performed in an anodizing plant showed in Figure 2.1b.



(a)



(b)

Figure 2.1: (a) PLH120 DC Power Supply 120V 0.75A. (b) LTC Caoduro anodizing plant.

Once the sample and electrolyte were prepared, the electrochemical cell was set up. The electrolyte mixture was poured into a beaker after placing a titanium mesh on its internal wall that will act as the cathode, surrounding the *Ti* sample, the anode. The decision to implement a large surface area difference between the cathode and the anode was made to promote a more homogeneous distribution of current density, thus enabling more uniform oxide formation. As anticipated in paragraph 1.9.3, this configuration setup causes a uniform oxide layer growth over both surfaces of the *Ti* substrate. With the help of a conductive clamp, the anode was placed at the center of the cell, completely submerged in the electrolyte. In particular, the conductive clamp consisted of a small titanium rod bent to resemble pliers and covered by a non-conductive plastic sheath except for its tips and central region (Figure 2.2). The coating electrically isolates the arms of the clamping tool from the electrolyte, preventing it from being involved in the process and causing parasitic currents and bath contamination. The region of contact between the sample and the clamp must be very small and localized at the edges of the upper part of the film. This precaution allows the arms of the clamping tool not to shield part of the anode from

the electrolyte, without the risk of leaving some regions not anodized or a non-uniform oxide layer.



Figure 2.2: Illustration of the conductive clamping tool.

Figure 2.3 illustrates a complete cell setup, with red conductive cables connecting the clamping tool and the titanium mesh to the anode and cathode of the power supply, respectively.

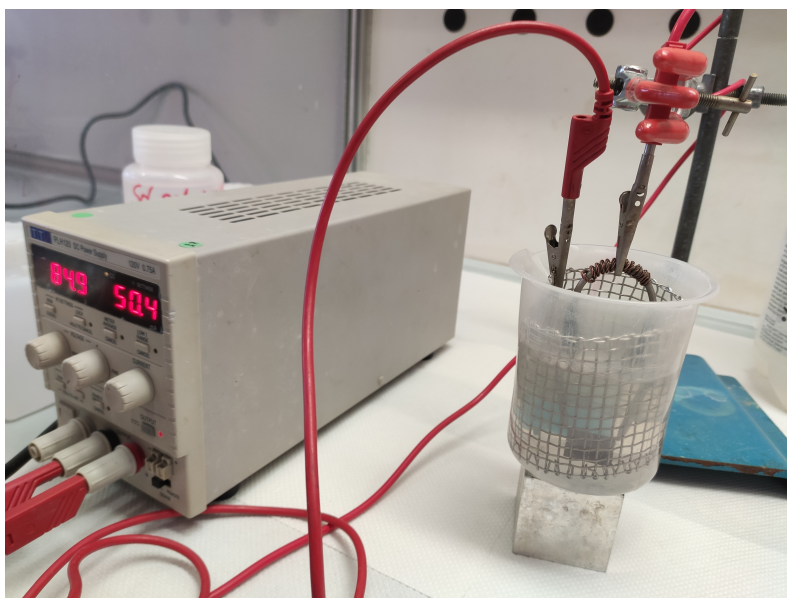


Figure 2.3: Complete setup of an electrochemical cell in a galvanostatic plant.

2.1.4. Synthesis of TiO_2 nanotubes

In paragraph 1.9.4, it was hinted that a multi-step anodic oxidation approach promotes the growth of highly ordered self-organized hexagonal TiO_2 nanotubes; therefore, this was

the strategy chosen in previous research works to develop the photocatalytic membranes. During the experiments performed in galvanostatic mode, the power supply current output was regulated to flow inside the sample a current density of 11 mAcm^{-2} , while avoiding an excessive voltage fixed above 90 V. In the potentiodynamic plant, the sample was anodized with a potential difference between the electrodes fixed at 45 V and reached with a voltage ramp of 2 V per second. Regardless of the conditions for anodization, the total time allowed for the growth of the first oxide layer was 30 minutes. Below, Figure 2.4 shows the electrical parameters selected on the display of the potentiodynamic chamber and the output regulation on the power supply.

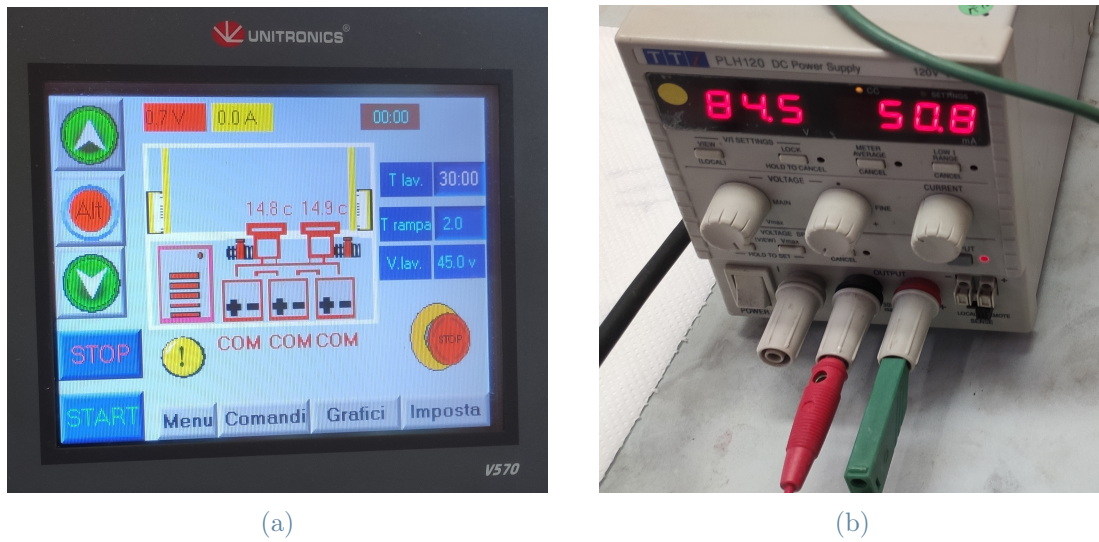


Figure 2.4: (a) Control panel in LTC Caoduro anodizing plant. (b) PLH120 DC Power Supply with its current output regulated to the desired value.

Once the first galvanostatic anodization was finished, the sample was rinsed with ethylene alcohol and water to wash away electrolyte traces. Then, it was ultrasonically cleaned with 1 M hydrochloric acid solution for 20 minutes in order to dissolve the first layer and leave only hexagonal imprints on the surface for promoting the organized growth of the second layer. Afterwards, a second cleaning step was performed in the sonic chamber with distilled water to remove any acidic residues from the sample.

When the component was ready for the second anodization, the electrochemical cell was set up again with the same electrolyte and electrical parameters. However, for the second oxidation in galvanostatic conditions, the anodization time was extended for 2 hours. At the end of this process, the surface of the *Ti* sample, originally with a shiny silver color, featured a dark gold appearance due to the growth of oxide on its surface. Figure 2.5 highlights this notable difference before and after the double anodization. In particular,

this layer presented a brighter color after the first anodization; still, after the longer second step, the oxide had grown thicker, causing a small variation in its interaction with light and subsequently emerging with a darker shade.

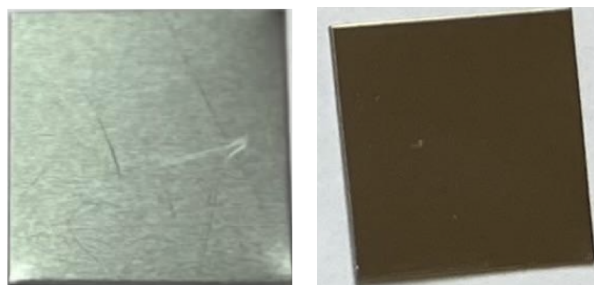


Figure 2.5: Difference in color of a *Ti* sample before and after double step anodization process.

Again, after this step, the sample is rinsed with ethylene alcohol and distilled water and then dried with compressed air very gently in order not to break the new oxide layer.

2.1.5. Thermal annealing

After double-step anodization under galvanostatic conditions or single-step potentiodynamic oxidation, the next step of the process is the thermal annealing treatment, where the sample was placed inside the oven for 2 hours at 450°C in ambient atmosphere. This temperature is sufficient for promoting the complete crystallization of amorphous TiO_2 into the anatase phase, as seen in paragraph 1.9.1. Figure 2.6 offers a frontal view of the equipment used for this phase, a GEFRAN 1200 oven, and its internal porous ceramic walls that leave enough space for heating multiple samples at the same time. In particular, in order to limit the risk of damaging the samples from direct contact with the walls, they were carefully placed on stacked ceramic plates, shown in Figure 2.7, and left hanging by their edges to limit the untreated area.



Figure 2.6: Frontal view of a GEFTRAN 1200 oven and its inner room surrounded by ceramic porous walls.

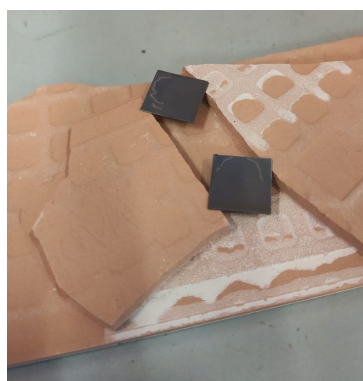


Figure 2.7: Stacked ceramic plates upon which the anodized samples are placed for thermal annealing.

From the last picture, it is also evident that the color change of the samples after thermal annealing is a preliminary visual effect of the crystallization.

2.1.6. Detachment for free-standing membranes synthesis

The strategy adopted for synthesizing free-standing nanotubular membranes consisted of two steps. The first one involved the electrochemical growth of a new amorphous

oxide layer between the substrate and the crystallized oxide. This third anodic oxidation process was performed in galvanostatic conditions, following the same parameters and time interval as the first anodization. This approach was anticipated in paragraph 1.9.5, where a thermal treatment was hinted at aiding in the membrane detachment from the substrate. Indeed, the different etching resistivity between the amorphous and crystalline layers can be exploited for a simpler and more efficient detachment.

For the second step of this phase, the samples were immersed in a petri dish with 1 M HCl solution and left overnight to ensure neat separation of top anatase TiO_2 nanotubes. The next day, the dish was gently stirred to move away the membrane from the substrate while gradually pouring the acidic solution into its bottle (Figure 2.8). After obtaining two films in acceptable conditions, small fragments and broken pieces were washed away with ethylene alcohol.

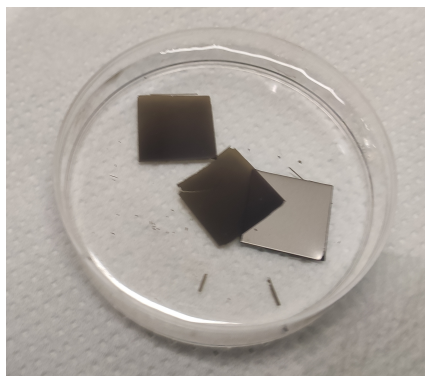


Figure 2.8: Chemical detachment in 1 M HCl solution for free-standing TiO_2 nanotubular membranes.

If at the end of the process the Ti sample possessed good surface quality, the substrate was reused for the growth of another nanotubular oxide layer starting from the second anodization step after rinsing it with ethylene alcohol and distilled water.

2.2. Photocatalytic degradation characterization tests

Photocatalytic tests were performed on both anodized Ti substrates and free-standing TiO_2 membranes to evaluate the photocatalytic performances on organic contaminants degradation. In the next paragraphs, the experimental setup for photodegradation and the equipment used to evaluate the organic dye concentration over time will be discussed.

2.2.1. Preparation of the photodegradation test setup

These experiments involved the use of a magnetic stirring machine for enhanced homogeneity of the solution during photodegradation. The solution chosen to simulate the contaminated water source contained an organic dye, such as 10^{-5} M Rhodamine-B. A small quantity of this mixture, 40 *mL*, was poured into beakers with a maximum capacity of 100 *mL*. In order to avoid direct contact between the magnetic stirrer and the catalyst that would cause serious damage to the latter and hinder the rotation of the stirrer, each substrate was placed on top of a U-shaped titanium net for support. Free-standing membranes were carefully dropped on an additional thin titanium net (Figure 2.9), whose shape can be modeled to fully cover the beaker diameter to avoid excessive re-arrangement of the membrane during the experiment due to their intrinsic fragility.



Figure 2.9: Image of thin titanium net where free-standing membranes were deposited.

The UV irradiation of the photocatalyst was provided by Nichia NCSU033B (T) UV SMD-LEDs, characterized by an emission intensity focused on the near UV. Each UV-LED was mounted on a 3D printed plastic circular support and positioned atop the beakers with weights to ensure tight sealing and prevent contamination from the ambient atmosphere. The LEDs were electrically connected in series and powered by the Potentiostat Model 2051, regulated to emit 0.5 A. Regarding the magnetic stirrer, this equipment possesses six working stations, each having a different magnetic field strength, causing a slight variation in the stirrer speed. To account for this problem that can inhibit the reproducibility of the experiment when dealing with multiple samples, each beaker needed to be switched in place with a different one every hour for 6 times, the total number of working stations. Finally, once the stirring speed was set at 300 rpm and the power supply of the LEDs was switched on, photodegradation of the organic dye was initiated. The complete setup is illustrated below in Figure 2.10.

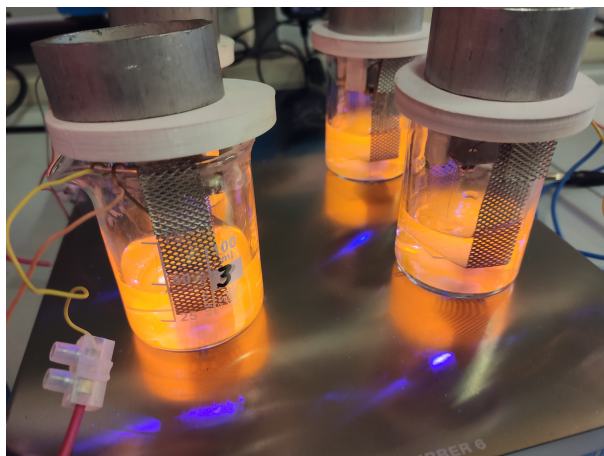


Figure 2.10: Complete setup for photocatalytic degradation tests of aqueous solution with 10^{-5} M Rhodamine-B under UV irradiation.

2.2.2. Measurement approach for photodegradation assessment

As anticipated in the previous paragraph, the membranes were left to degrade the organic dye solution for one hour before changing the beakers' positions. Before repeating the tests, a small volume of the mixture was taken and poured into plastic cuvettes for the successive step in photocatalytic characterization tests. It consisted of measuring the absorbance of the dye solution after every one hour through a spectrophotometer SPECTRONIC 200E (Figure 2.11).



Figure 2.11: Image of the spectrophotometer SPECTRONIC 200E.

Inside the spectrophotometer, there's a support for a cuvette to be irradiated with incident light in the range of 340-1000 nm (Figure 2.12a). After previous calibration with a cuvette filled with water, the machine was able to provide the exact value of absorbance by recording the intensity of transmitted light.



Figure 2.12: (a) Image of the cuvette holder inside the spectrophotometer. (b) Example of absorbance spectrum exhibited on the display of the spectrophotometer.

As seen in Figure 2.12b, the display of the spectrophotometer highlights the absorbance of the solution near its absorption spectrum. From this value, the residual concentration of the organic dye in the solution after photodegradation can be calculated with the Lambert-Beer law:

$$A = \varepsilon l C \quad (2.1)$$

in which A is the absorbance, ε is the absorption coefficient, l is the optical path length and C is the concentration of the organic dye. As the concentration is measured every hour after photocatalysis tests, it is possible to obtain a graphical trend of its value over time with the formula used for the kinetic model of pseudo-first-order reactions:

$$\ln \frac{C}{C_0} = -k t \quad (2.2)$$

where C_0 is the initial concentration of Rhodamine-B, k is the reaction constant and t is the reaction time. It is evident from this equation that in the case of efficient photodegradation, the concentration decreases over time, and the trend is reflected as a straight line with a negative slope equal to $-k$. Additionally, the reaction constant can be exploited for determining the most efficient photocatalytic performance when comparing different samples.

2.3. Quantum dot loading

In this section, the preparation steps for depositing quantum dots on free-standing TiO_2 nanotubular membranes and anodized Ti substrates will be discussed. After preparation, the loaded samples followed the same experimental approach described above to evaluate the final photocatalytic performance, intending to observe an improvement compared to the samples before quantum dot loading.

2.3.1. Experimental procedure for deposition of quantum dots

From the Università di Trieste unit, two populations of quantum dots in the form of powders were delivered to the Politecnico di Milano unit, one consisting of $CdSe/CdS$ core-shell nanoparticles, while the other of $CdSe$ core-only quantum dots. These powders were previously poured inside the centrifugal filter unit, shown in Figure 2.13, and wrapped with Parafilm very tightly before transport. Upon arrival, each unit was weighted to evaluate the effective mass of quantum dots and so their initial volume.



Figure 2.13: Image of the centrifugal filter unit before being weighed.

The drop-casting technique was the chosen method to deposit the quantum dots on the photocatalytic layers, with ethanol as the solvent due to its rapid evaporation rate and good surface wettability on TiO_2 . Three different batches were prepared for assessing the effect of the two different populations of quantum dots on the free-standing membrane and nanotubular oxide still bonded to the Ti substrate. These batches, each characterized by various combinations of nanoparticles and ethanol respective volumes, are reported below:

Table 2.1: Batch 1: Core-shell quantum dot (CsQD)-loaded TiO_2 membranes, this batch is for assessing the photocatalytic performance of TiO_2 membranes according to the core-shell quantum dot concentration.

Sample	CsQD Volume (μL)	Ethanol Volume (μL)
TCS-5-a	5	35
TCS-15-a	15	25
TCS-35-a	35	5
TCS-5-b	5	35
TCS-15-b	15	25
TCS-35-b	35	5

Table 2.2: Batch 2: Core-only quantum dot (CoQD)-loaded TiO_2 membranes. In this batch, the photocatalytic performance of TiO_2 membranes was evaluated depending on the core-only quantum dot concentration.

Sample	CoQD Volume (μL)	Ethanol Volume (μL)
TCo-5-a	5	35
TCo-15-a	15	25
TCo-35-a	35	5
TCo-5-b	5	35
TCo-15-b	15	25
TCo-35-b	35	5

Table 2.3: Batch 3: Quantum dot loading on anodized Ti substrate (TS), in this batch, the Ti substrates were oxidized with a single-step anodization in potentiodynamic conditions at 45 V for 30 minutes and then annealed at 450 °C for 2 hours.

Sample	QD + Ethanol Volume (μL)
TSCs-A	40
TSCs-B	40
TSCo-A	20
TSCo-B	20

As it is shown in these tables, samples with specific volume ratios between quantum dots and ethanol were repeated to assess the reproducibility of the experiments. Each sample was subsequently subjected to centrifugation using a centrifugal machine with dedicated tubes for inserting the filter units. The speed was set to the maximum value for one hour to disintegrate large aggregates and poorly dispersed particles. At the end of the process, the units presented a small deposit at the bottom and a homogeneously dispersed solution, from which only a precise volume fraction was withdrawn and deposited on top of the membranes. Finally, during solvent evaporation at room temperature, the quantum dots were able to bond within the nanotubes through surface interactions.

3 | Results and discussion

This chapter reports the experimental results covering the synthesis and characterization of free-standing TiO_2 nanotubular membranes. Regarding the fabrication phase, careful examination has been conducted to assess the quality of the samples after every step toward chemical detachment, and the procedures followed to overcome unwanted issues will be discussed in detail. This chapter also includes data from the photocatalytic assessment tests performed on free-standing membranes and oxidized Ti substrates. The last section will cover photodegradation outcomes after quantum dot loading to provide a clear evaluation of its consequences on samples.

3.1. Discussion on defects encountered during synthesis of free-standing membranes

The main part of this research work entailed the assessment of the reproducibility of free-standing membranes synthesis following the parameters and reagents that were refined in previous laboratory activities. As an example, Figure 2.8 illustrates the detachment phase of one of the first two samples realized, showing a uniform and square specimen with no missing pieces or fragments.

However, one of the first problems encountered in this project arose when synthesizing new samples with a new electrolyte. Despite following the same reagents, the just-prepared electrolyte yielded more fragile membranes, causing small areas of the oxide layer to fall off from the substrate during cleaning and drying operations, even with very low pressures applied (Figure 3.1).

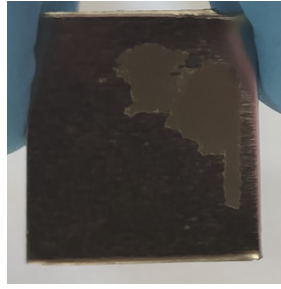


Figure 3.1: Image of a double-step anodized Ti substrates after cleaning and drying operations. The gold-colored central region is the remains of the oxide layer, which broke into small fragments despite the low pressure applied.

The brittleness of the oxide film also caused major problems during and after thermal treatment. After annealing in the oven at 450°C for 2 hours, some layers detached early from the substrate, leaving the Ti substrate unprotected against the high temperature environment. Following the annealing step, mechanical removal of the useless exfoliated oxide areas was conducted with the help of small pliers, while gently tapping the ceramic support to push away any residual fragments or debris. In one of the worst cases, almost half of the entire oxide layer was destroyed, leaving an irrelevant amount on the substrate for the third anodization step. Meanwhile, the exposed zone of the Ti substrate appeared with blue and violet nuances. This effect was attributed to thermal oxidation of the exposed Ti substrate after the delamination of the main oxide film. A visual representation of the issue discussed above is given in Figure 3.2.



Figure 3.2: Visual representation of the condition of three fragile TiO_2 layers after annealing. Surrounded by small fragments and debris, the remaining films appear curled up due to the different thermal stresses of the oxide layer compared to the metallic substrate.

In order to account for the missing pieces present in those samples, it was decided to

proceed with the third anodization step with specimens whose oxide layer was uniform for at least 70% of the substrate surface. This decision was also made in order to avoid the risk of discarding too many samples, as one of the first deadlines of the project was to send enough membranes to the Università di Trieste unit for further research. Thanks to this approach, it was possible to deliver more than 6 membranes in acceptable conditions, along with two square membranes yielded by the perfect sample previously mentioned. Up to this point, all samples started as 1.5 cm X 1.5 cm squares of *Ti* and then anodized in galvanostatic conditions for all three steps of electrochemical oxidation. In order to cope with the enhanced brittleness of new oxide layers, one of the first strategies was to employ an older electrolyte utilized by researchers in previous anodization experiments. However, the same issue of oxide detachment mentioned above occurred again before annealing. After multiple experiments in galvanostatic conditions, illustrated in Figure 3.3, it was observed that the breakage of nanotubular TiO_2 was mainly localized around the clamping region. Due to this aspect, it was first suggested that the clamping force exercised by the clamping tool on the substrate was too excessive during the longest anodization step. Nonetheless, the main cause of the problem was attributed to the fact that the electrolyte was probably near the end of its service life, and therefore inhibited in developing oxide layers strong enough to withstand even small pressures.

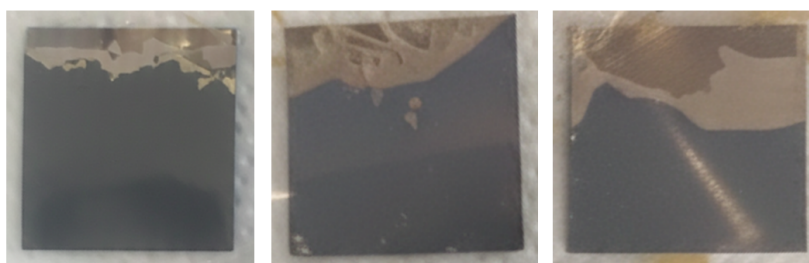


Figure 3.3: Image of 2.5 cm X 2.5 cm *Ti* samples oxidized by a double-step anodization process with an old electrolyte of the same compounds but utilized in previous research work.

Three other samples were realized with this electrolyte but oxidized with a single-step anodization process in potentiodynamic mode. Probably due to the short operation time compared to the second anodization phase, the oxide layers didn't present any signs of early detachment and fragments, and for two of them, photocatalysis characterization tests were performed, and the results will be discussed in the next section.

Meanwhile, a second electrolyte was prepared by mixing the electrolyte implemented so far to produce the membranes delivered to Trieste with the one that yielded the most perfect free-standing membrane achieved so far. Figure 3.4 shows the three samples

yielded from this electrolyte. The first two followed a double-step anodization process in galvanostatic mode, and, at the end, they presented serious damage along the clamping region. As anticipated before, the most probable cause was the adoption of a mixture of very exhausted electrolytes. In addition, it was observed that the solution temperature after one hour of operation was alarmingly high. After analyzing the state of the first two samples, the third one was stored after a single anodization step, and the absence of defects on its surface drew closer attention toward the longer, second anodization phase.

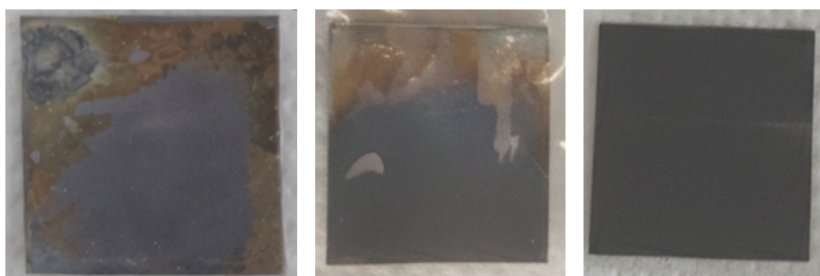


Figure 3.4: Image of 2.5 cm X 2.5 cm *Ti* samples oxidized by a double-step anodization process with an electrolyte fabricated by mixing the newly prepared electrolyte with the one that yielded the most perfect free-standing membrane.

Unfortunately, the samples produced from a new electrolyte exhibited the same issue as the first samples obtained from the previous electrolyte. Indeed, after annealing, the oxide layers produced from double step anodization process in galvanostatic conditions were too brittle, and, as highlighted in Figure 3.5, after removing all the loose fragments on the surface, only half of the surface was still covered by thick TiO_2 .

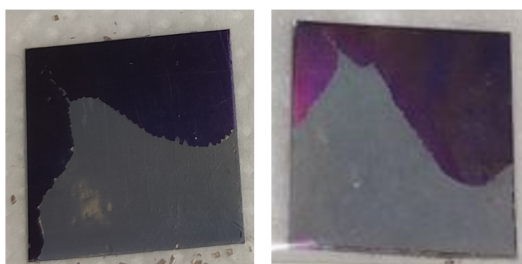


Figure 3.5: Images of 2 cm X 2 cm *Ti* samples oxidized by a double-step anodization process with a fresh electrolyte.

In addition, a new defect occurred while producing new samples with the same electrolyte. After the second anodization step, along the lateral sides of the substrate, thin, elongated, irregular regions appeared. As shown in Figure 3.6, these flowed areas possess a dark gold

color, which differentiates them from the dark gray appearance of perfect TiO_2 present at the center of the sample.

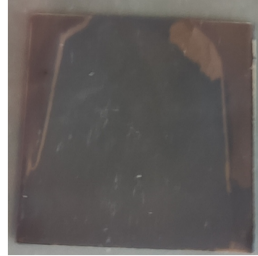


Figure 3.6: Image of a 2 cm X 2 cm anodized Ti sample exhibiting two lateral, flawed, golden regions in contrast with the classic dark gray color of TiO_2 .

As can be expected, after annealing, the oxide layer was severely damaged, as shown in the samples of Figure 3.2. In particular, the most compromised regions were located in the same position as the darker, defective areas observed before thermal treatment.

To exclude any possible superficial defects on the original Ti substrate that would cause the above mentioned issue, two new samples were tested after undergoing mechanical polishing treatment. Despite that, the one oxidized following the traditional three-step anodization process in galvanostatic conditions showed an oxide coating seriously fractured after annealing, after observing the presence of those faulty regions. The same outcome afflicted two non-polished samples despite implementing a newer electrolyte. A close-up image of these last samples is reported in Figure 3.7, while being less evident than those exhibited in Figure 3.6, the faulty sections are separated from the pristine oxide layer by the same pale yellowish lines.



Figure 3.7: Close-up image of two 2 cm X 2 cm samples before annealing, exhibiting pale yellowish lines that map the compromised area after the second anodization.

All electrochemical oxidation processes were initially performed under direct current conditions, with the anodization voltage rapidly rising to 90 V when aged electrolytes were employed. However, due to the issues encountered, a less aggressive approach was adopted for the anodization of the second polished *Ti* substrate, which was carried out in potentiodynamic mode. Under these conditions, the voltage was gradually incremented to 45 V with a ramp of 2 V s^{-1} , enabling a progressive increase in the potential difference, and consequently of the electric field, to promote a more controlled oxide growth. As the sample didn't show any superficial flaws after annealing, it was decided to anodize further polished substrates in potentiodynamic conditions.

Before that, two new membranes were fabricated to observe any anomaly when following the three-step anodization process with the parameters for electrochemical oxidation in the LTC plant. Although no defects arose after the second anodization and annealing steps, the detachment phase was problematic as the membranes couldn't be easily detached after leaving the samples in 1M *HCl* solution overnight. Eventually, once the layers were peeled off and left to dry, they emerged as very thin and fragile.

Concurrently, new membranes from non-polished *Ti* substrates were manufactured in galvanostatic conditions with a new electrolyte to collect multiple samples to study under photocatalytic tests. During the fabrication of this last batch of TiO_2 nanotubular layers, most of them exhibited darker, compromised sections delineated by pale lines. This is the same issue mentioned earlier, and it was also observed to occur more frequently in the clamping regions, with only one occasion of it being located at the opposite side. Despite discarding many samples before the third anodization phase, an acceptable number of membranes for subsequent tests was achieved, and are illustrated in Figure 3.8, which also shows the specimens that were further anodized despite the defects due to a uniform oxide layer for more than half of their surface area.

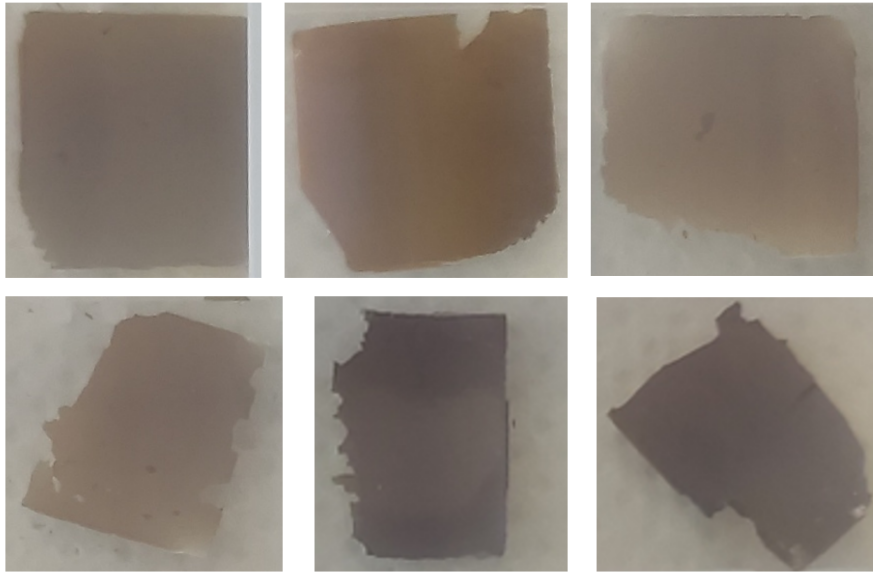


Figure 3.8: Free-standing TiO_2 nanotubular membranes synthesized under galvanostatic conditions following the three-step anodization process.

Before covering the results obtained from the photocatalytic performance tests on both free-standing membranes and anodized substrates, the next section will discuss the possible causes of all the defects encountered in this thesis work.

3.1.1. Discussion on the causes of the observed defects

Following the discussion of the main defects encountered during the synthesis of free-standing TiO_2 membranes, this section will describe the possible underlying causes behind their appearance.

The first problem was the enhanced brittleness of the oxide layers fabricated with fresh electrolyte, which caused the early detachment of some of its portions and subsequent fragmentation. The reason for this issue can be easily identified in the freshly prepared electrolyte and the ions present during the electrochemical process. As described in section 1.9.3, the dissolution of the initial TiO_2 compact oxide layer arises from the formation of water-soluble complex $[TiF]^{-2}$ due to the interaction between free F^{-} anions and H^{+} with Ti^{4+} cations ejected at the oxide-electrolyte interface. While the concentration of the fluoride complex increases over repeated electrochemical processes, the amount of free F^{-} and H^{+} ions reduces, thus inhibiting the dissolution step in aged electrolytes [37].

Furthermore, the electrical conductivity decreases as it is proportional to the F^{-} and H_2O content in the electrolyte. Usually, in a fresher, conductive electrolyte, the establishment of the electric field around the anode is promoted, thereby reaching the set voltage, which

is the value corresponding to the equilibrium between oxide formation and its dissolution, at a stable current density in a short time. On the contrary, in a less-conductive aged electrolyte, the process took more time to reach this equilibrium, exhibiting a "plateau" in the current-time plot, highlighting the initial interval when the voltage slowly increases towards its set value.

Interestingly, this delay can be correlated to the formation of thicker layers. In aged electrolyte, as the Ti^{4+} cations, still released in high numbers, interact with fewer F^- anions, there will be fewer fluoride complexes at the interface, allowing the oxidic layer to grow towards greater thicknesses. Meanwhile, with a fresh electrolyte, the higher concentration of free fluoride ions yields more water-soluble complexes, causing the rapid dissolution of the still-growing TiO_2 layer. Guo et al. observed how a swift balance between the oxide coating formation and dissolution could determine the growth of disordered nanostructures with hindered stability. Despite this fact, proceeding with further anodization processes permitted the electrolyte to develop stable and self-ordered nanopores, confirming the benefits of the aged electrolyte [74]. Figure 3.9 offers a schematic illustration for understanding the contrast in chemical composition in fresh and aged electrolyte, as well as a recap table to overview the key differences between the two.

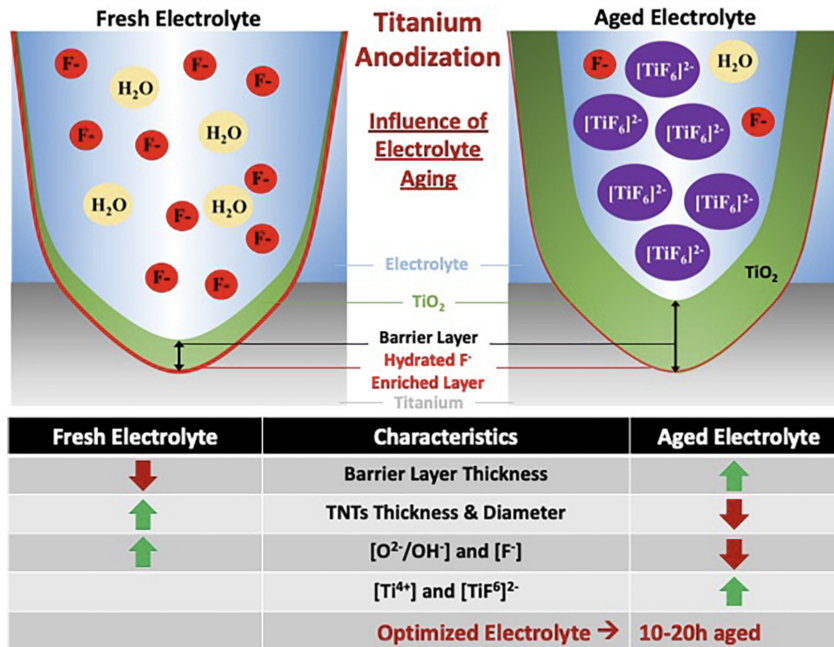


Figure 3.9: Anodization of titanium in fresh and aged electrolyte and the key differences in electrolyte chemical balance and the fabricated titania nanotubes [37].

Furthermore, another important parameter that changes over repeated anodization processes is the pH of the electrolyte. Its significance originates from its capacity to influence

the TiO_2 geometry of the nanotubes that was observed in different studies. Indeed, scientists concluded that the growth of self-ordered titania nanotubular layers with increased pore diameter and small wall thickness can be favored with the implementation of an electrolyte whose pH value is in a neutral range ($\approx 7-8$) [75]. However, a fresh, slightly acidic electrolyte, with a high amount of H^+ ions, will enhance the oxide dissolution rate, determining the occurrence of defects, such as cracks and instabilities, in the base layer that trigger a non-uniform distribution of internal stresses. This effect was observed by Gulati et al. during their research for the optimization of the anodization parameters for the growth of titania nanotubes, and confirmed the favorable effect of electrolyte aging on the stability of nanotubes [38]. Considering the morphology of the anodic film, to highlight its structural stability, Gulati's research group analyzed the SEM images of anodized Ti wires manufactured from fresh and aged electrolyte (Figure 3.10). While the fresh electrolyte yielded TiO_2 nanotubes with numerous cracks and evident delamination from the substrate, from the implementation of the second electrolyte, aged after 10 hours of anodization tests, scientists achieved a stable and adherent nanotubular oxide layer.

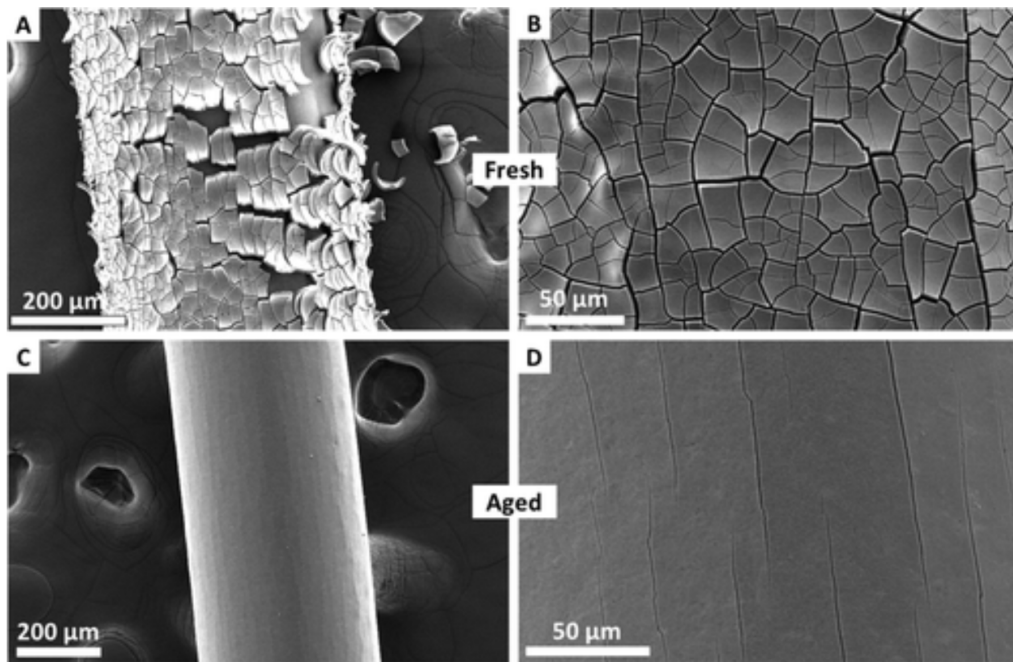


Figure 3.10: Low and high-resolution SEM images of anodic films for anodization performed in (a,b) fresh and (c,d) aged (10 h) electrolytes. Anodization was performed at 75 V for 10 minutes using ethylene glycol/ NH_4F electrolyte with 1% in volume of water [38].

Despite the advantages mentioned above, the implementation of aged electrolyte over a fresh one still carries the risk of producing damaged nanostructures, especially when the

mixture is near the end of its life. The consequences of an exhausted electrolyte were mentioned in the previous section and shown in Figure 3.4. In order to provide a detailed explanation for the sample state after anodization in this condition, it's fundamental to consider two important parameters, such as the electrolyte temperature and the anodization voltage.

After every anodization process performed in galvanostatic conditions with the same electrolyte, the value of the set voltage read on the power supply increased. When a fresh electrolyte was employed, the maximum voltage stabilized at approximately 68 V, consistent with the field supporting effect introduced by lactic acid, which enables a higher anodization voltage to promote the growth of longer and more robust nanotubes without being limited by dielectric breakdown phenomena. However, as the electrolyte progressively aged, the steady-state voltage exceeded 90 V, a threshold value initially established in this work as an indication of an unusable electrolytic solution.

This phenomenon can be traced back to the decrease in conductivity of the electrolyte. According to Ohm's law, the potential difference between the two electrodes is proportional to the flowing current multiplied by the resistivity of the electrolyte. In particular, this last quantity is inversely related to the conductivity and therefore to the presence of F^- and H_2O species in the electrolyte. As their concentration decreases after each anodization step due to the formation of water-soluble complexes, the resistivity of the solution is enhanced, and the system, to maintain a constant current density, is forced to augment the anodization voltage.

An higher potential difference has a positive effect on the formation of a nanotubular structure, as many studies confirmed [76]. Having a direct influence on the growth rates of nanotubes, the anodization voltage plays an important role as it determines the establishment of the electric field that drives ion migration in the electrolyte during the process. Unfortunately, ion mobility is hindered by another factor, the viscosity of the electrolyte. As mentioned in paragraph 1.9.2, a small quantity of water is required for lowering the rheological behavior of the mixture, thus facilitating the flow of ions. However, as water molecules are consumed by hydrolysis reactions to generate H^+ ions, the overall charge transport is further impeded, and the system is obliged to raise the potential difference again, dangerously approaching the threshold value for dielectric breakdown.

Before continuing with the explanation of this mechanism, it's important to make a brief digression to discuss the role of the temperature of the electrolyte. Scientists confirmed that this quantity was capable of changing the length of the nanotubes, the wall thickness, and the oxide growth rate [77]. After studying the effect of different electrolyte temperatures on nanotube morphology, various research works concluded that an optimal growth of self-ordered TiO_2 nanotubular layers was favored at room temperature (20-25

°C). Indeed, in one of those studies, Ocampo et al. noticed the presence of defective areas on the oxide surface while analyzing the morphology of anodized *Ti* samples, which are illustrated in Figure 3.11.

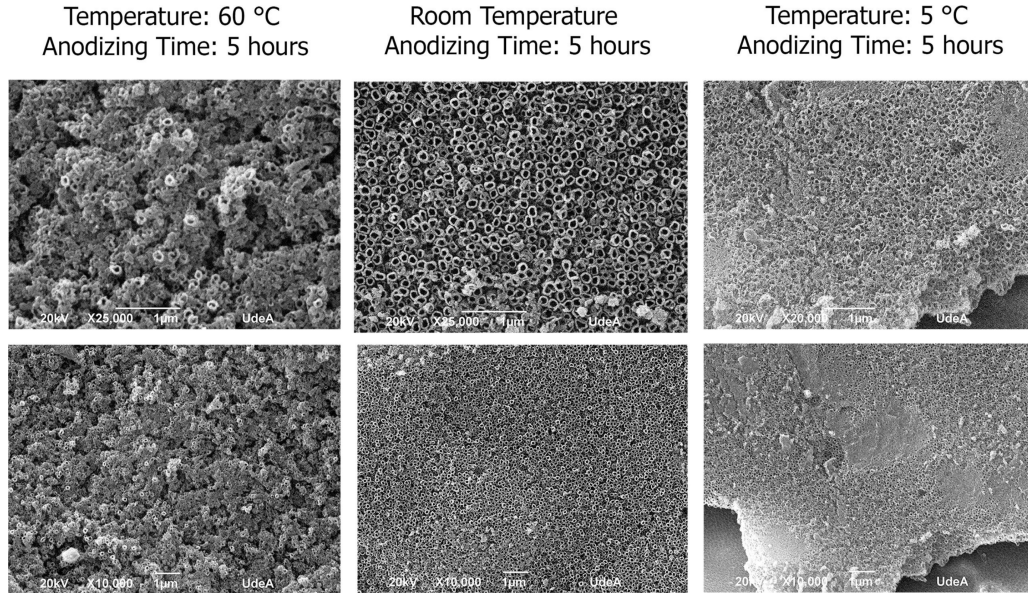


Figure 3.11: SEM images showing the temperature electrolyte effect on nanotube morphology of anodized *Ti* samples in aqueous electrolyte [39].

Ocampo's group attributed this temperature effect to the variation of the electrolyte viscosity that affects the nanotube morphology, as anticipated before. As the temperature increases, the viscosity drops, provoking a non-homogeneous dissolution during anodization, and the final layer exhibited both nanotubular and compact oxide areas. At low temperatures, despite achieving well-defined nanotubes, the dissolution rate wasn't sufficient and caused the formation of oxide particles at the tip of the nanotubes [39].

This digression was fundamental to introduce another aspect that stimulates the system to move towards the dielectric breakdown, the self-heating characteristic of a nearly exhausted electrolyte. As the solution ages, becoming less viscous and conductive, the voltage of the system increases as well as its resistivity, and these two factors significantly enhance the energy dissipated during the process, according to the following formula:

$$P = V I = I^2 R \quad (3.1)$$

where P is the electrical power dissipated from the system, V the voltage, I the flowing current, and R the resistivity of the electrolyte and of the oxide layer. This energy is dispersed in the form of heat that increases the temperature of the electrolyte. In ad-

dition to this, as the overused solution is less chemically stable than a fresh one, this heating step can be non-uniform, and the temperature may rise rapidly and with less control. As mentioned earlier, at higher temperatures, the viscosity drops, causing irregular dissolution rates and hindering the overall charge transport, forcing the system to further amplify the voltage. However, once its value surpasses the threshold for dielectric breakdown, very high local current densities on the *Ti* substrate are triggered, causing a significant increase in temperature for the small areas affected by breakdown phenomena [78]. Below are described the principal effects observed once the anodized *Ti* samples reached this stage:

- The collapse of the nanotubes and subsequent loss of the self-ordered morphology;
- Partial delamination of the oxide from the metallic substrate;
- Formation, induced by the electric field, of non-visible micro-sparks capable of burning the oxide layer, thus leaving burned areas on the surface of the sample at the end of the process.

Figure 3.12 provides a more detailed view of the samples shown in Figure 3.4 obtained from mixing two nearly exhausted electrolytes. Compared to the first image, the samples had been stored for months after the second anodization step, and during their placement inside plastic bags, some portions of the oxide layer easily detached and exhibited the underlying *Ti* substrate. The dark yellow areas observed on the surface correspond to regions of altered TiO_2 after dielectric breakdown, where the nanotubular structure collapsed.



Figure 3.12: Close-up image of the two samples obtained from the mixture of two nearly exhausted electrolytes, highlighting the defects originating from dielectric breakdown phenomena.

From these observations, it is evident how the samples yielded with overused electrolyte were practically unusable for further experiments and therefore discarded, as well as the anodization solution.

The discussion for the last part of this section will be focused on the mechanism responsible for the occurrence of those elongated defective regions that have been highlighted in Figure 3.6 and Figure 3.7. The main factor determining this defect can be identified in an intrinsic problem of the electrochemical cell configuration. As other studies demonstrated, the difference in distance from the counter electrode, the titanium mesh, between the lateral sides of the sample and its center leads to a non-uniform distribution of the electric field [79]. As a result, the local current density in those regions reaches higher values, giving rise to augmented heat dissipation on the borders of the samples. While with the implementation of a fresh electrolyte, the system is able to withstand this phenomenon, an aged electrolyte is capable of amplifying it.

As mentioned above, to support a constant current flow with a less conductive solution, the system is forced to increase the potential difference between the electrodes, therefore enhancing the electric field. Hence, the local current density on the borders intensifies. In addition, as the temperature of the electrolyte rises due to energy dissipation in the system, local heating of the borders is further boosted. At this stage, the growth of a regular and stable nanotubular structure on the lateral sides of the substrate is not promoted anymore, leading to the appearance of those defective, dark gold regions, in contrast to the more uniform, gray colored oxide located at the center. Considering this, the opaque lines can be characterized as the boundaries of the transition between the regime that followed uniform nanotube growth and the one characterized by intensified local heating. Figure 3.13 offers a clear view of two other samples exhibiting this issue.

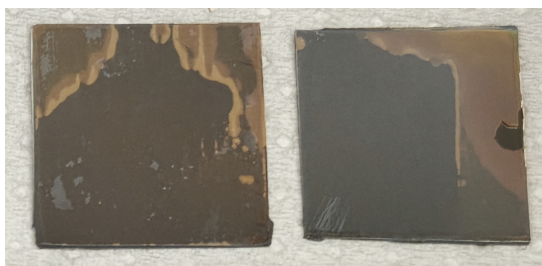


Figure 3.13: Close-up image of two samples showing the dark, gold layer where regular nanotubular structure growth was hindered by the amplification of the local temperature at the lateral zones. It can also be noticed that the elongated opaque lines delimitate these defective areas.

In order to cope with the rise of the local temperature at the borders of the sample, the adopted strategy was to produce the standard electrolyte in higher volumes for the purpose of changing the warm solution after every anodization step with a colder one, especially after the long, second phase of oxidation.

3.2. Analysis on photocatalytic performance

3.2.1. Data elaboration

Before listing the experimental results from the photocatalysis characterization tests performed in this research work, this section serves as a detailed explanation of the process of data elaboration followed for each tested sample. As described in section 2.2.2, after every hour of photodegradation tests, a small volume of organic dye solution was taken and filled inside a cuvette to measure the absorbance value on the spectrophotometer, as shown in Figure 2.12b. For each cuvette, the measurements were repeated three times in order to collect a more representative average value. Then, by exploiting the Lambert-Beer law and the formula for the kinetic model of pseudo-first-order reactions, also known as the Langmuir-Hinshelwood equation, the natural logarithm between this quantity and the initial absorbance value was calculated. Finally, the results were plotted against time to visualize their trend, as schematically illustrated in Figure 3.14, for example.

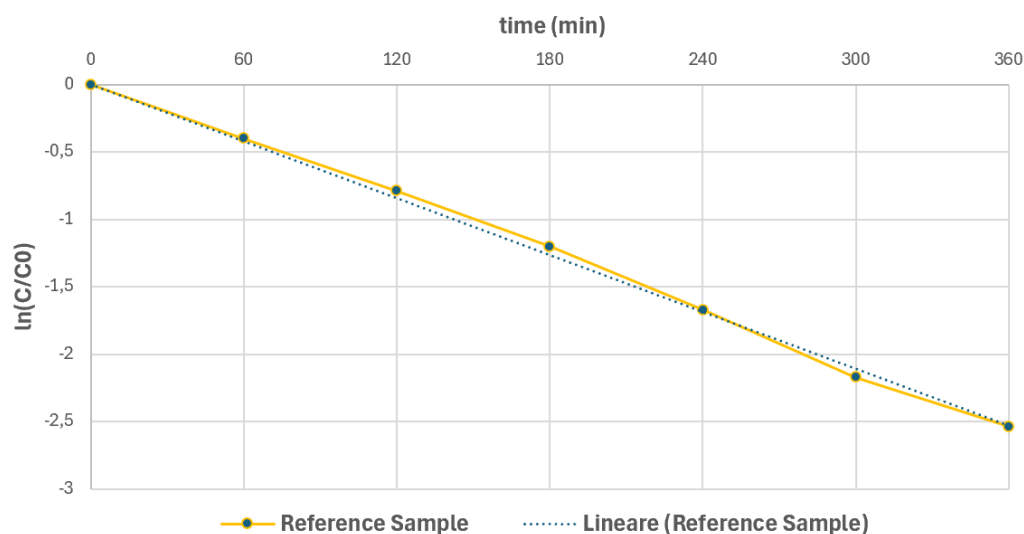


Figure 3.14: Exemplary schematic illustration of Rhodamine-B concentration plot against time during photodegradation tests based on the equation for the kinetic model of pseudo-first-order reactions.

From a preliminary visual inspection, the obtained curve closely follows its linear regression, confirming the hypothesis of describing the results from the photodegradation test with an equation for a pseudo-first-order kinetic reaction model. Thanks to this property, it was possible to derive the constant reaction rate k of degradation from the slope of the linear regression. When evaluating the photocatalytic property of multiple samples,

this value was normalized to the photocatalyst surface area under light irradiation for a proper comparison.

3.2.2. Photocatalysis tests on anodized *Ti* substrates

One of the first evaluations on the photodegradation capability of anodized *Ti* substrates was performed on two 2.5 cm X 2.5 cm samples, S1 and S2, due to the absence of defects on their surface, as showcased in Figure 3.15. As previously mentioned in paragraph 3.1, these specimens were obtained from a single-step anodic oxidation in potentiodynamic conditions followed by thermal annealing.

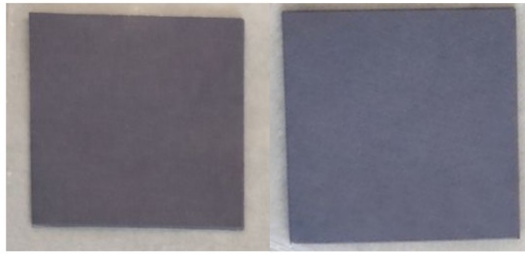


Figure 3.15: Anodized *Ti* substrates after single-step anodization in potentiodynamic conditions and thermal annealing.

As anticipated in the previous section, by exploiting the Langmuir-Hinshelwood equation, it was possible to derive two curves by plotting the natural logarithm of the ratio between the final and initial absorbance values of the organic dye against time. Table 3.1 presents a table summarizing the absorbance values measured hourly from photodegradation tests with the two samples, while Figure 3.16 offers a graphical representation of the curves as well as their linear regression.

Table 3.1: Rhodamine-B absorbance values measured hourly during photodegradation tests performed on two anodized *Ti* substrates after annealing.

Minutes	S1-Absorbance	S2-Absorbance
0	1	0.996
60	0.669	0.695
120	0.454	0.473
180	0.300	0.297
240	0.188	0.195
300	0.114	0.118
360	0.079	0.077

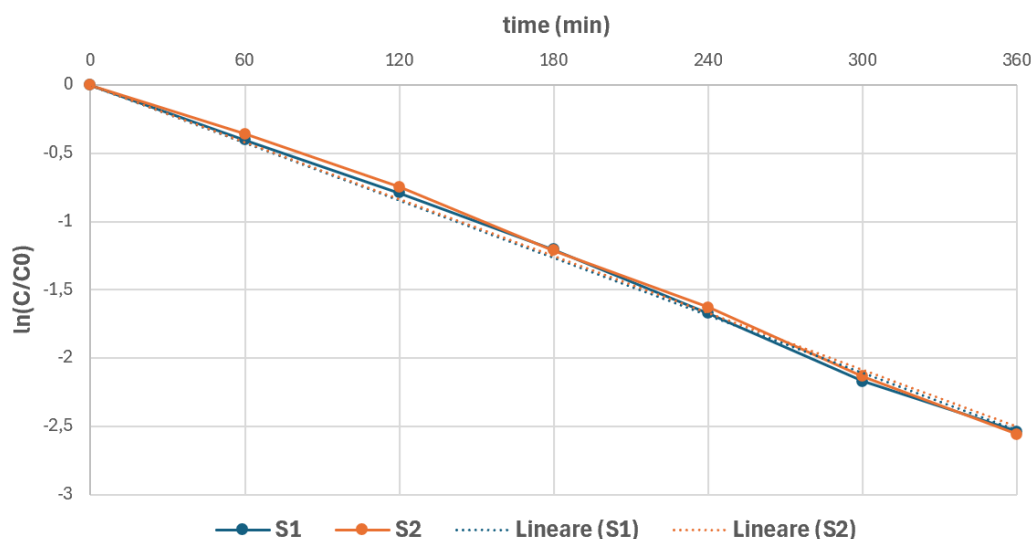


Figure 3.16: Plot of the Langmuir-Hinshelwood equation and its linear regression for the two anodized substrates derived by taking the concentration of the organic dye every hour.

Some conclusions are obtained from the observation of the graph above. The negative slope of the two curves highlights the efficacy of the two anodized substrates in degrading the organic dye, with its concentration reaching values much lower than zero after six hours, leaving a transparent mixture, very different from the pink colored initial solution. Finally, from the linear regression, the reaction rate constants were derived and normalized to the surface area of the substrates. Both samples yielded the same optimal specific constant reaction rates, such as $1.6 \times 10^{-3} \text{ min}^{-1} \text{ cm}^{-2}$, confirming the reproducibility for the development of anodized substrates in these working conditions.

3.2.3. Photocatalysis tests on free-standing TiO_2 membranes

Following the standard three-step electrochemical anodization process, six free-standing TiO_2 nanotubular membranes were fabricated and subjected to photocatalysis characterization tests. Although some of these samples, shown in Figure 3.8, exhibited evident damage as a result of the issues discussed previously, photodegradation experiments were still carried out to evaluate the specific reaction rate constants and ensure a fair comparison. As for the case with anodized Ti substrates, the table below offers the absorbance values measured for each sample hourly (Table 3.2), while Figure 3.17 illustrates the related curves derived from the Langmuir-Hinshelwood law and their linear regression.

Table 3.2: Rhodamine-B absorbance values measured hourly during photodegradation tests performed on free-standing TiO_2 nanotubular membranes.

Minutes	T1-Abs	T2-Abs	T3-Abs	T4-Abs	T5-Abs	T6-Abs
0	1.03	1.02	1.04	1.038	1.03	1.049
60	0.79	0.798	0.82	0.839	0.859	0.828
120	0.629	0.606	0.60	0.744	0.763	0.667
180	0.474	0.446	0.452	0.652	0.66	0.559
240	0.342	0.329	0.35	0.583	0.577	0.465
300	0.259	0.24	0.273	0.49	0.50	0.398
360	0.206	0.175	0.215	0.416	0.409	0.345

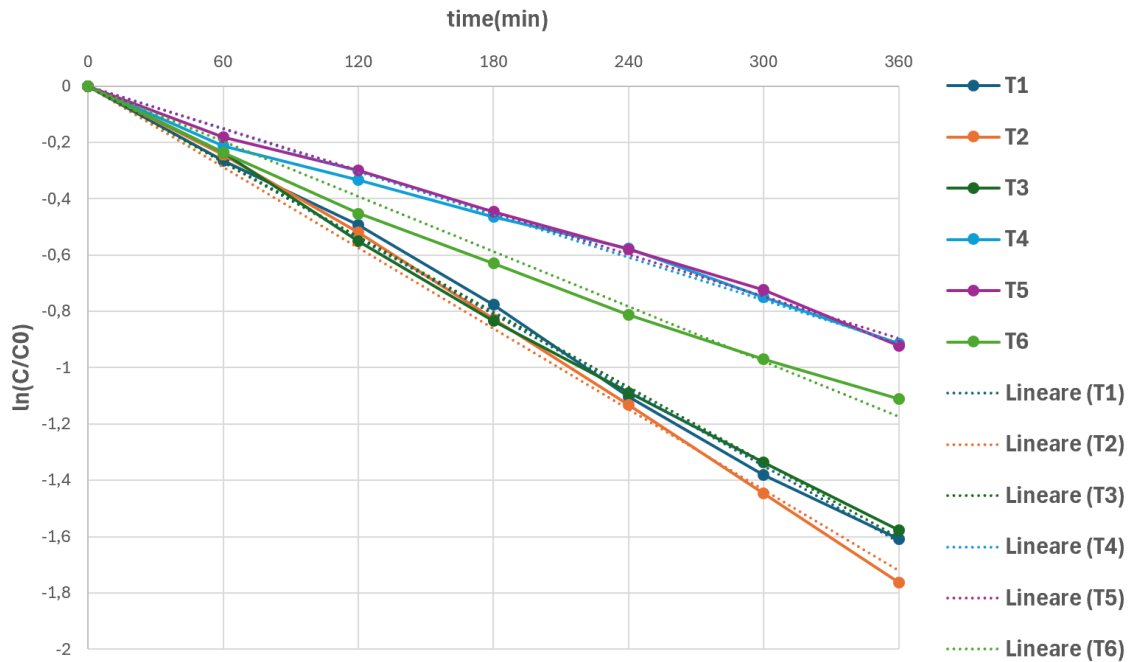


Figure 3.17: Plot of the Langmuir-Hinshelwood law and its linear regression for each of the six membranes derived by taking the concentration of the organic dye every hour.

Compared to the graph illustrated in Figure 3.16, the curves obtained from photodegradation tests performed on free-standing membranes appear less linear, with more scattered data points. This behavior represents an important indicator of the quality and reliability of the photocatalysis test. While in the experiments performed on anodized Ti substrate, the oxide layer was uniform throughout the measurements, free-standing membranes were more difficult to handle due to their intrinsic fragility. As a result, some of them appeared fragmented into small pieces at the end of the process, as shown in Figure 3.18.

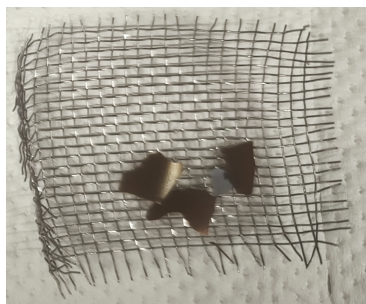


Figure 3.18: State of a free-standing TiO_2 membrane after six hours of photodegradation tests, appearing fragmented into small pieces.

Although this issue resulted in a slower photodegradation kinetics of the self-standing membranes compared to the anodized substrates, the final specific reaction rate constants, reported in Table 3.3, showed encouraging results for photocatalysis characterization, as some of these values were even higher than those obtained for the oxide layers still bonded to their substrates.

Table 3.3: Specific reaction rate constants ($k_{specific}$) for each free-standing TiO_2 nanotubular membrane tested.

Sample	$k_{specific} [\text{min}^{-1} \text{ cm}^{-2}]$
T1	2.08×10^{-3}
T2	2.20×10^{-3}
T3	2.27×10^{-3}
T4	1.61×10^{-3}
T5	1.83×10^{-3}
T6	2.25×10^{-3}

3.3. Assessment on enhanced photocatalysis through quantum dot loading

To evaluate the photocatalytic performance of both free-standing membranes and anodized substrate after quantum dot loading, the same photodegradation characterization procedures previously applied for samples without nanoparticles was followed. Figure 3.19 and 3.20 show the two graphs illustrating the trends derived from the Langmuir-Hinshelwood law and the relative linear regression of the absorbance values measured from the first two batches of quantum dot loading.

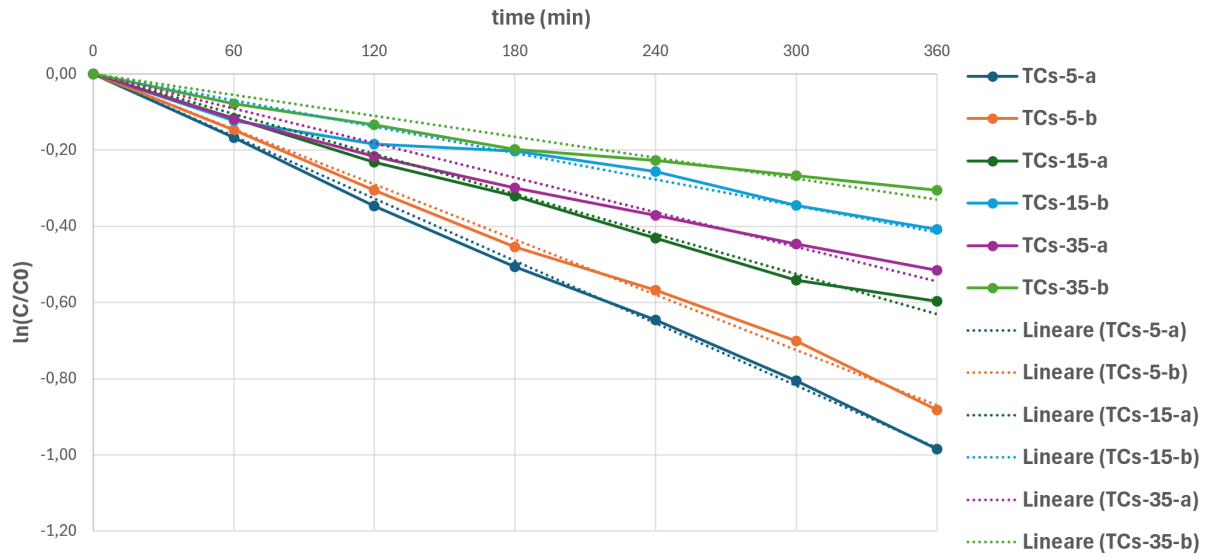


Figure 3.19: Trend of Langmuir-Hinshelwood law and the relative linear regression of the absorbance values measured from photodegradation tests performed on free-standing TiO_2 membranes loaded with $CdSe/CdS$ core-shell quantum dots.

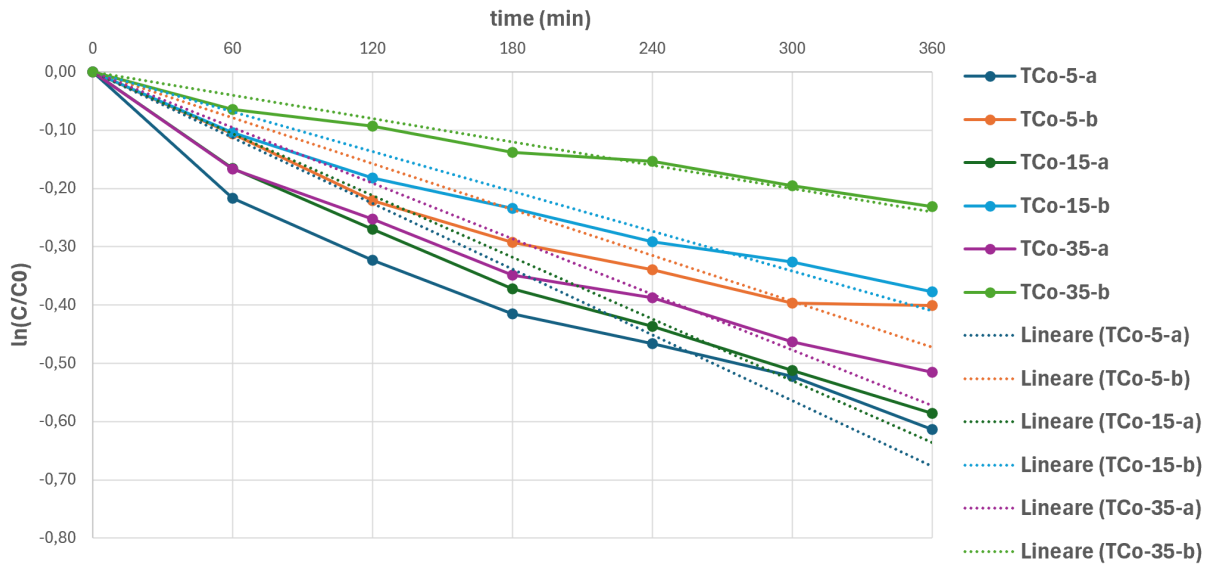


Figure 3.20: Trend of Langmuir-Hinshelwood law and the relative linear regression of the absorbance values measured from photodegradation tests performed on free-standing TiO_2 membranes loaded with $CdSe$ (core-only) quantum dots.

As anticipated in the previous paragraph, handling free-standing membranes comes with the intrinsic issue of their structural fragility, which often leads to fragmentation during photodegradation tests. This effect resulted in scattered data and negatively affects the

reliability of the experiments. Nonetheless, from the results obtained from photocatalytic degradation tests, it was possible to evaluate the specific reaction rate constants ($k_{specific}$) normalized to the surface area of each tested sample. These values, which offer a quantitative view of the photodegradation efficiency, have been reported in the graph below in Figure 3.21.

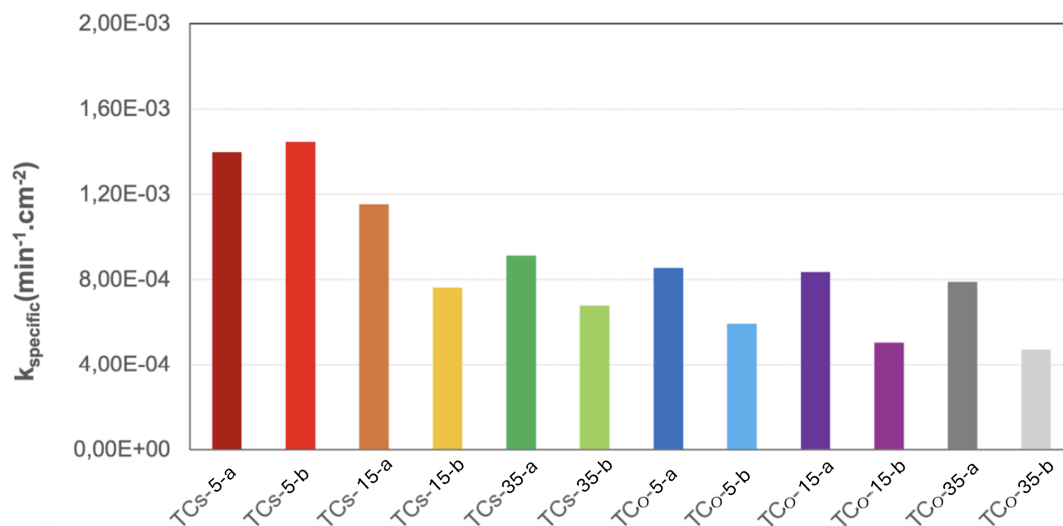


Figure 3.21: Comparison between the specific reaction rate constants of the first two batches, where core-shell and core-only quantum dots have been loaded on free-standing membranes.

Before discussing in depth the outcomes derived from the graph above, the results determined from photodegradation tests performed on anodized *Ti* substrates loaded with both core-shell and core-only quantum dots are presented below. In particular, Figure 3.22 illustrates the trend of the data calculated before and after quantum dot loading to provide a clear visual comparison of the enhancement in photocatalytic activity achieved through this surface modification technique.

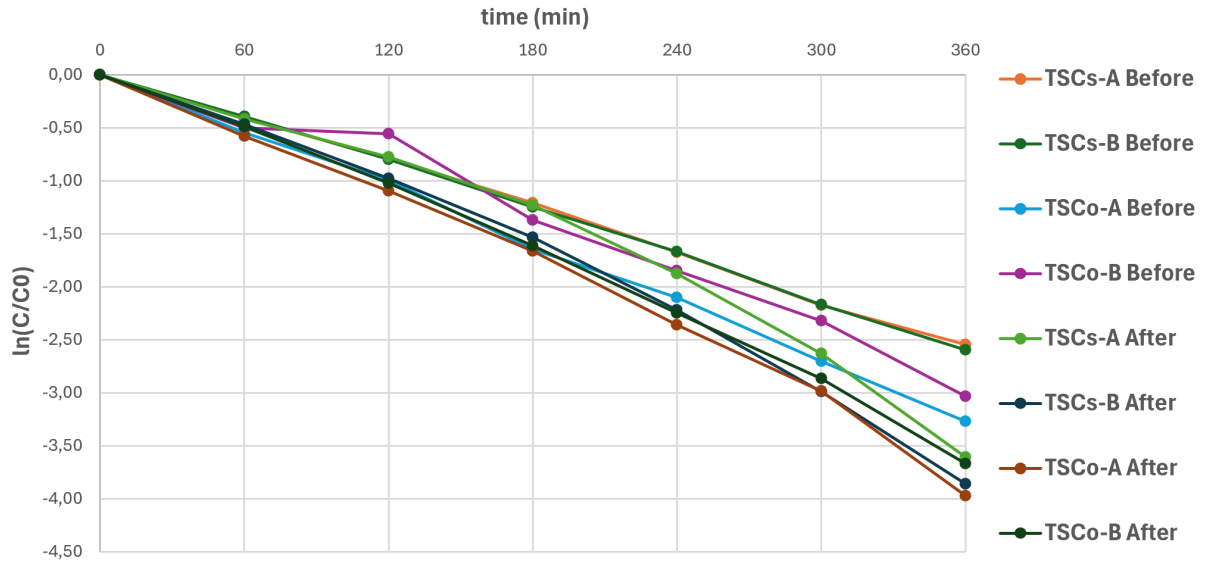


Figure 3.22: Trend of Langmuir-Hinshelwood law of the absorbance values measured from photodegradation tests performed on anodized *Ti* substrates before and after both core-shell and core-only quantum dot loading.

Finally, the specific reaction rate constants derived from the linear regression of the curves illustrated above have been reported in the following graph (Figure 3.23).

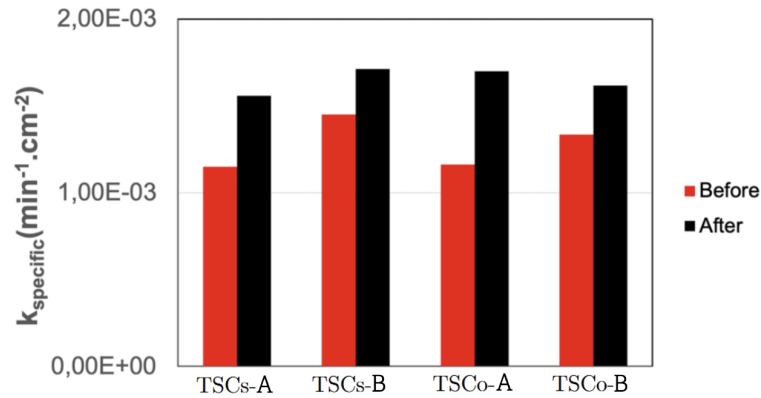


Figure 3.23: Comparison between the specific reaction rate constants of the third batch with anodized *Ti* substrates before and after quantum dot loading.

3.3.1. Comparison between core-shell and core-only quantum dots

Figure 3.21 depicts a clear difference between the $k_{specific}$ values of the core-shell QD-loaded samples from their core-only-loaded analogues. The first batch outperformed the

second one while also highlighting an optimal loading range fixed at lower volumes like $5\ \mu\text{L}$. As an example, while the highest values reported for the samples TCs-5-a and TCs-5-b were $1.40 \times 10^{-3}\ \text{min}^{-1}\ \text{cm}^{-2}$; conversely, the most efficient sample of the second batch, TCo-5-a, demonstrated a considerably lower reading of $8.54 \times 10^{-4}\ \text{min}^{-1}\ \text{cm}^{-2}$.

The improved performance of quasi-type 1 core-shell quantum dots compared to core-only nanocrystals can be justified through other projects focused on the characterization of these nanostructures. As discussed in paragraph 1.9.4, coupling TiO_2 with a narrow bandgap semiconductor has proved to be an optimal solution for limiting recombination phenomena as well as promoting electron transfer towards titanium dioxide for efficient light harvesting and consequently enhanced photocatalytic activity [80]. Nonetheless, quasi-type 1 CdSe/CdS core-shell nanocrystals were synthesized by the Università di Trieste unit specifically to act as an electron source for TiO_2 . Indeed, in this configuration where core and shell have staggered bandgaps, as CdSe absorbs visible light, creating an exciton, rapid migration of the photogenerated electron towards CdS occurs. This behavior enables a more efficient charge separation, extending the lifetime of the exciton compared to the situation with core-only quantum dots. Then, due to the relative position of the conduction bands in TiO_2 and CdS , the photogenerated electrons are swiftly transported to the nanotubes for subsequent oxidizing species formation.

As for the optimal loading range of quantum dots identified at the lowest volume employed in this experiment, such as $5\ \mu\text{L}$, the cause can be attributed to the risk of nanotube clogging. Since the photocatalytic activity of TiO_2 is intrinsically related to the availability of its surface to participate in the oxidation of organic contaminants, excessive concentrations of quantum dots likely promote their aggregation inside nanotubes, blocking their openings. This phenomenon can hinder light penetration, charge transport, and mass diffusion within the photocatalyst, consequently reducing its efficiency, as observed for loading volumes of $15\ \mu\text{L}$ and $35\ \mu\text{L}$.

Regarding the reproducibility of the experiments, despite the encouraging outcomes obtained from TCs-5-a and TCs-5-b, noticeable deviations were registered between the samples with different loading volumes of quantum dots and their counterpart. As a preliminary analysis, the cause was attributed to a higher sensitivity to slight variations during the drop-casting technique or superficial defects on the membrane. Moreover, the discrepancies in specific reaction rate constants were more pronounced in less efficient samples, highlighting the reduced reliability of the measured data due to intensification of the intrinsic errors of the experimental procedure.

3.3.2. Influence of quantum dot loading on anodized *Ti* samples

Significant improvements in the photocatalytic performance were also reported for quantum dot-loaded anodized *Ti* samples, independent of the type of quantum dots. As documented in Table 3.4, the gap between core-shell and core-only QD loading is smaller compared to the results from the comparison between the first two batches. In addition, the greatest relative improvement was achieved by TSCo-A, a core-only QD-loaded sample. The significant enhancement in the photodegradation efficiency on anodized substrates emphasized the versatility of this surface modification approach, even without membrane detachment.

Table 3.4: Comparison of k_{specific} values before and after treatment and the relative percentage increase.

Sample	k_{specific} (before) [$\text{min}^{-1} \text{ cm}^{-2}$]	k_{specific} (after) [$\text{min}^{-1} \text{ cm}^{-2}$]	Relative increase (%)
TSCs-A	1.15×10^{-3}	1.56×10^{-3}	35.7
TSCs-B	1.45×10^{-3}	1.71×10^{-3}	17.9
TSCo-A	1.16×10^{-3}	1.70×10^{-3}	46.6
TSCo-B	1.34×10^{-3}	1.62×10^{-3}	20.9

3.3.3. Further investigations on quantum dot loading

As all the photocatalytic characterization tests performed so far exhibited insufficient reproducibility, a fourth batch of quantum dot loading was prepared to compare the specific reaction rate constants after surface functionalization with both core-shell and core-only quantum dots. In particular, the samples loaded were 2 cm X 2 cm *Ti* squares oxidized with a single-step anodization in potentiodynamic conditions at 45 V for 30 minutes and then annealed at 450 °C for 2 hours. While the nanocrystals involved in these tests had the same composition as the ones employed in the previous tests, their loading volumes were reduced towards lower values (0.05, 0.25, 0.5, and 5 μL) to further confirm the hypothesis that nanotube clogging hinders the photocatalytic performance of the system.

Figure 3.24 and 3.25 illustrate the Langmuir-Hinshelwood trends derived from the data collected during photocatalysis experiments performed on the differently functionalized substrates.

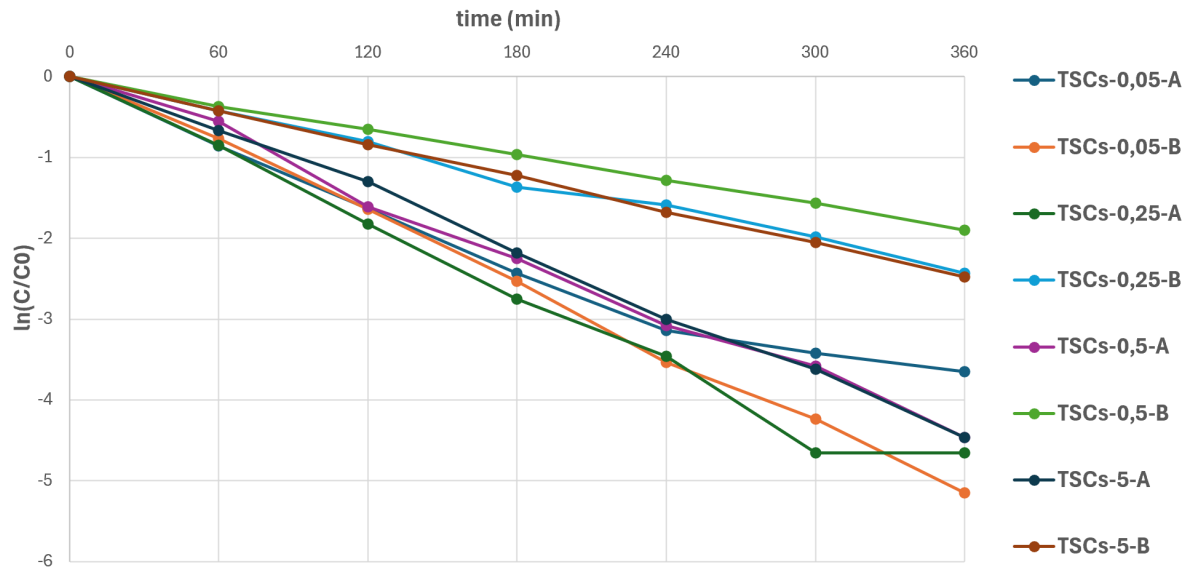


Figure 3.24: Trend of Langmuir-Hinshelwood law of the absorbance values measured from photodegradation tests performed on anodized *Ti* substrates loaded with *CdSe/CdS* core-shell quantum dots.

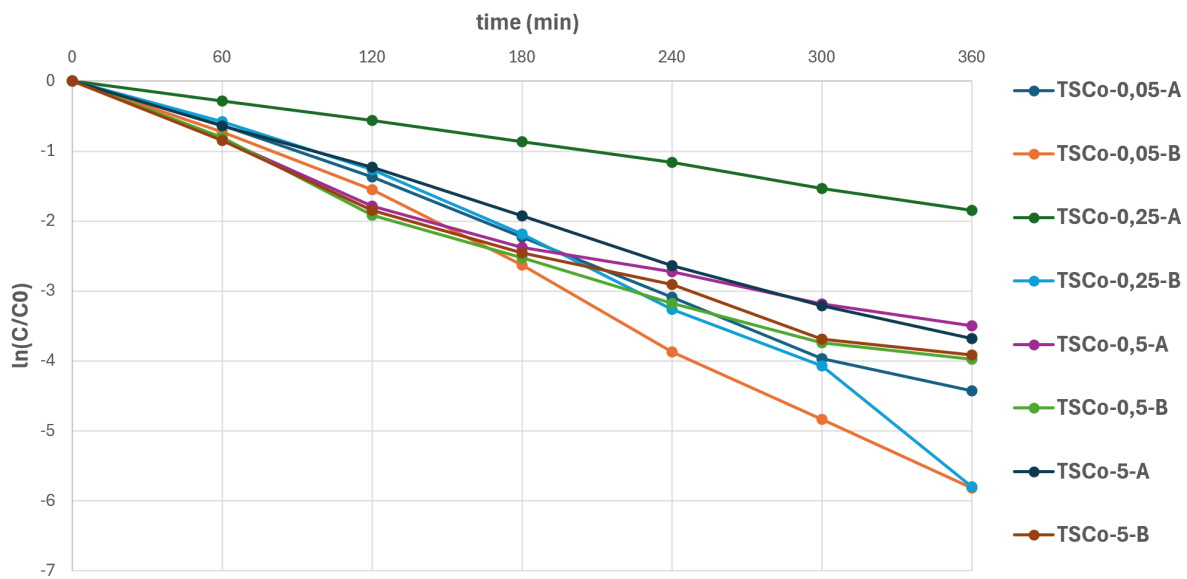


Figure 3.25: Trend of Langmuir-Hinshelwood law of the absorbance values measured from photodegradation tests performed on anodized *Ti* substrates loaded with *CdSe* (core-only) quantum dots.

Figure 3.26 reports the specific reaction rate constants obtained from the linear regression of the curves previously illustrated, to provide a visual comparison of the photodegradation efficiency of the tested samples.

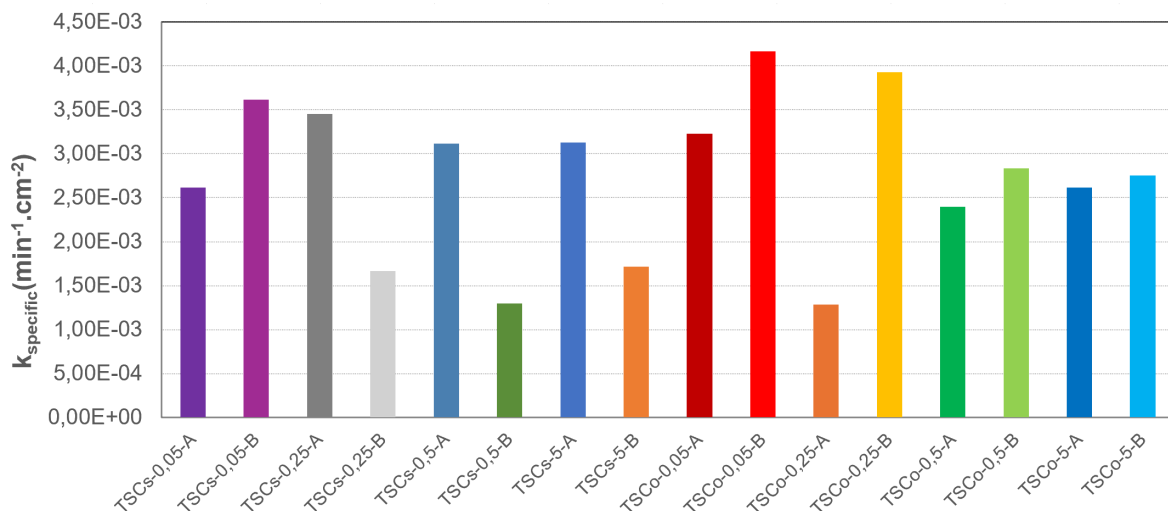


Figure 3.26: Comparison between the specific reaction rate constants of the fourth batch of quantum dot loading, where core-shell and core-only nanoparticles have been loaded on anodized *Ti* substrates.

Several samples exhibited high specific reaction rate constants, with the highest peak reaching $4.17 \times 10^{-3} \text{ min}^{-1} \text{ cm}^{-2}$ for the sample loaded with $0.05 \mu\text{L}$ of core-only quantum dots. Notably, the maximum constants for both core-shell and core-only systems were obtained at the lowest loading volume, further validating the hypothesis that excessive nanoparticle concentration may induce nanotube clogging and consequently reduce photocatalytic performance.

However, despite confirming the strong enhancement in photocatalytic activity induced by surface functionalization, the results showed evident discrepancies between samples prepared under identical conditions. This variability highlights the limited reproducibility of the drop-casting technique, whose high sensitivity to deposition parameters may lead to non-uniform nanoparticle distribution and aggregation inside the nanotubes. Therefore, these outcomes suggest that further optimization of the loading procedure is required to achieve improved control over the functionalization process.

4 | Conclusions and future developments

The primary goal of this thesis work regarded the synthesis of free-standing TiO_2 nanotubular membranes for future integration in interfacial solar evaporator systems with the aim to degrade, by means of photocatalysis, organic pollutants present in water. Therefore, photocatalytic characterization tests were performed on both free-standing membranes and anodized Ti substrates to ascertain the ability of the oxide layer in decomposing the Rhodamine-B content of a water-based solution. As the main research project is also interested in the synergistic interaction between the photocatalytic property of TiO_2 combined with quantum dots as photoabsorbers, both their deposition onto the oxide layers and additional degradation tests were carried out to confirm this phenomenon.

Free-standing TiO_2 nanotubular membranes were fabricated through a multi-step electrochemical anodization process on Ti substrates under galvanostatic conditions or via a single-step anodic oxidation performed under potentiodynamic conditions. Both the electrical and chemical parameters implemented were derived from previous research works that analyzed their influence on the morphology of the nanotubes. While synthesizing multiple samples to assess the reproducibility of the process, defects were observed on samples after the second and most time-consuming anodization step, from which the final oxide layer thickness was obtained before thermal treatment. All the defects have been attributed to the state of the electrolyte, and this correlation was confirmed with the experimental results analyzed in the previous chapter. Indeed, electrolyte aging emerged as a critical factor influencing the anodization process, as its progressive degradation altered the steady-state voltage, affected the oxide formation, and consequently compromised the structural stability and uniformity of the nanotubular layer. Through iterative anodization experiments and confrontation with the existing literature, the electrolyte usage was optimized to achieve the reliable fabrication of free-standing membranes.

In contrast to the issues encountered on anodization step, the photocatalysis characterization tests demonstrated encouraging results. In fact, when placed under UV-light radiation, both free-standing TiO_2 membranes and anodized Ti substrates exhibited efficient degradation of the organic dye with optimal reaction rate constants. These outcomes are in line with the data collected in previous studies focused on titania due to its great photodegradation capability, non-toxicity, and high chemical stability. These experimental findings also support the reliability of the production of new TiO_2 membranes in these working conditions for future water purification applications.

Positive outcomes were also achieved from photodegradation tests performed on samples after quantum dot loading. In particular, when deposited on free-standing membranes, the core-shell quantum dot population has demonstrated higher photocatalytic activity compared to core-only quantum dots. The greatest improvements were observed with samples loaded with lower volumes of nanoparticles, which helped in determining an optimal loading range of approximately $0.25 \mu L$. As significant enhancements were measured while testing quantum dot-loaded anodized Ti substrates, the experiment also highlighted the efficacy of this surface modification approach even with the oxide layer still bonded to the substrate.

Through all these conclusions, this thesis work offers a useful insight into the limitations of the process for the synthesis of TiO_2 nanotubes by electrochemical oxidation, highlighting the critical factors that heavily influence the quality of the final structure. Nevertheless, the encouraging results obtained from photodegradation tests showed the viability of the process in producing systems for water purification purposes, while also confirming the enhancement in photocatalytic performance achieved through synergistic behavior between the oxide and quantum dots.

In the optics of future research works under the same project, their focus should be directed towards the following points:

- Further investigation on the factors influencing the growth of titania nanotubes during electrochemical anodization.
- Photocatalytic tests conducted on TiO_2 nanotubular membranes functionalized with semiconductor nanoparticles and integrated on a wooden floating substrate, to evaluate the performance of the complete solar evaporator.
- Optimization of the parameters adopted for the drop-casting technique to achieve an acceptable reproducibility in photocatalytic tests.

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