POLITECNICO
MILANO 1863

SCUOLA DI INGEGNERIA INDUSTRIALE
E DELL'INFORMAZIONE

Executive Summary of the Thesis

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

Laurea Magistrale in Materials Engineering and Nanotechnology - Ingegneria dei Materiali e delle Nanotecnologie

Author: Dennis Bulgarini

Advisor: Prof. Maria Vittoria Diamanti

Co-advisor: Begüm Aksu

Academic year: 2024-2025

1. Introduction

Climate change and environmental pollution are increasingly stressing global freshwater resources, representing an urgent issue for the sustainable development of modern society. Consequently, scientists are focused on the development of novel, energy-efficient technologies for advanced water purification. Among these, interfacial solar evaporators are an emerging solution to reduce pollution by harnessing solar energy to induce water evaporation followed by condensation into purified water [1].
However, the long-term reliability of these devices is hindered by salt accumulation, biofouling, and poor rejection of volatile and semi-volatile organic contaminants. While many research works have been devoted to solving the problem of low salt rejection, fewer papers have addressed the effective removal of organic compounds and biological fouling.
In this context, the incorporation of photocatalysts into solar-driven interfacial evaporators has been suggested as an effective strategy to activate light-induced oxidation for organic pollutant degradation and microbial inactivation [2]. Moreover, certain semiconductor photocatalysts are able to form a superhydrophilic layer on their surface under irradiation, thereby enhancing water transport and self-cleaning properties [3]. Recent studies have also observed a synergistic interaction between photothermal absorbers and photocatalysts, capable of enhancing the solar evaporator performances. Of the investigated materials, titanium dioxide (TiO_2) has been widely employed due to its great photodegradation capability, chemical stability, high refractive index, and non-toxicity [4].
This thesis was carried out within the framework of the COPE project, which proposes an innovative solar evaporator configuration combining semiconductor quantum dot photoabsorbers with free-standing TiO_2 nanotubular membranes integrated onto a self-regenerating wooden floating substrate. In particular, the synthesis of titanium dioxide layers through electrochemical oxidation and their photocatalytic performances have been evaluated both with and without quantum dot loading.

2. Materials and experimental procedures

Free-standing TiO_2 nanotubular membranes were synthesized through a three-step electrochemical anodization process under galvanostatic conditions, applying a current density of 11 $mAcm^{-2}$ to ensure controlled morphology and improved structural uniformity (Figure 1).

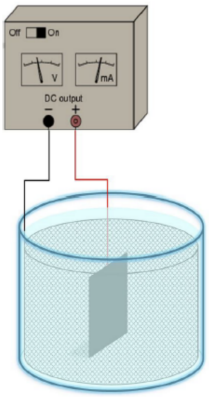


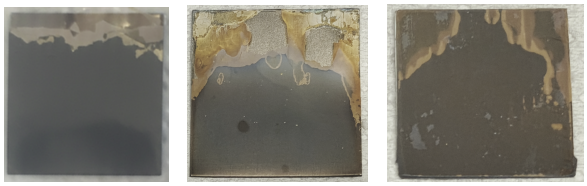
Figure 1: Experimental setup for titanium anodic oxidation.

The first anodization was conducted to form a sacrificial oxide layer, which was then removed to leave nanoimprints on the titanium surface that formed a template to favor the growth of highly ordered self-organized hexagonal TiO_2 nanotubes.
After the second anodization, thermal annealing was performed to promote the crystallization of the amorphous oxide layer into the anatase phase to improve the photocatalytic activity and mechanical integrity. Finally, a third anodization step was carried out to form an intermediate amorphous TiO_2 layer, whose different chemical etching resistivity compared to the crystalline oxide was exploited to achieve selective dissolution and the synthesis of free-standing nanotubular membranes suitable for integration into the solar evaporator system. In parallel, anodized Ti substrates were synthesized via single-step potentiodynamic anodization with a voltage ramp of 2 V per second up to 45 V, and maintained for 30 minutes.
For both conditions, the anodization process was carried out in a glycol-based electrolyte containing 0.1 M ammonium fluoride (NH_4F), 2 M distilled water (H_2O), and 1.5 M lactic acid ($C_3H_6O_3$) to ensure the growth of a self-organized nanotubular structure via the equilibrium between oxide growth and fluoride-assisted chemical dissolution.
The nanotubular morphology was selected due to its intrinsic advantages in photocatalytic applications, including enhanced charge carrier mobility, quantum confinement effects, and outstanding photon-harvesting capability. In addition, 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.
The photocatalytic performance was analyzed through photodegradation experiments carried out on the synthesized membranes and anodized substrates, which were immersed in an aqueous solution of Rhodamine-B, selected as a model organic contaminant, and irradiated under UV light. The degradation process was monitored via UV–vis spectrophotometry, exploiting the Lambert-Beer law to derive the dye concentration from the absorbance of the solution after every hour. Following the Langmuir–Hinshelwood model for pseudo-first-order reactions, the reaction rate constants of degradation were evaluated through linear regression of the experimental data, allowing the comparison of the photocatalytic efficiencies of the different systems.
In the last part of this thesis work, quasi-type I CdSe/CdS core–shell quantum dots (QDs) were employed as photosensitizers on TiO_2 membranes to enhance visible-light absorption and electron transfer toward the nanotubes for augmented photocatalytic activity. In parallel, CdSe core-only nanoparticles were applied to obtain a comparative assessment of the effect of the core-shell heterostructure on enhanced photocatalysis. Quantum dot loading on both free-standing layers was achieved through the drop-casting technique, and different QDs-to-ethanol ratios were used to determine an optimal loading volume. In addition, both core-shell and core-only quantum dots were deposited on anodized substrate to evaluate the versatility of this surface modification approach, even without membrane detachment.
The photocatalytic performance of the functionalized samples was assessed with the same photodegradation procedure before quantum dot loading.

3. Results and discussion

3.1. Critical aspects of electrochemical anodic oxidation

A systematic investigation of the anodization process observed the occurrence of morphological and structural defects under certain operating conditions. The first defect encountered was the pronounced brittleness of the oxide layers, which was associated with the use of a freshly prepared glycol-based electrolyte [5]. Although the growth of regular, self-ordered nanotubes is enhanced when the electrochemical system establishes an equilibrium between oxide formation and field-assisted dissolution, a fresh electrolyte favors excessive chemical etching. This imbalance determined the formation of a fragile oxide layer made of thin nanotubes with non-uniform morphology, particularly susceptible to delamination, as shown in Figure 2a. Furthermore, the slightly acidic character of the as-prepared solution contributed to mechanical instabilities and uneven distribution of internal stresses on the base layer.
From a comparison with the outcomes achieved from previous studies focused on optimization of the electrochemical parameters, an ideal time window of 10 hours for electrolyte aging was identified for achieving stable and regular nanotube growth. However, excessive electrolyte aging stimulated additional issues for anodization in galvanostatic conditions. As an electrolyte near the end of its usable lifetime loses part of its viscosity and electrical conductivity, the energy dissipated within the electrochemical cell is altered, resulting in a rapid temperature increase. Under these conditions, the system approached the dielectric breakdown limit, where elevated local current densities flowing through the oxide are triggered, disrupting the regular oxide formation. Consequently, the nanotubular structure partially collapsed, localized detachment of the oxide layer occurred, and the generation of micro-sparks led to burned regions of titanium dioxide (Figure 2b).
Moreover, the reduced chemical stability of the aged electrolyte intensified the local heating at the edges of the substrate, as the electric field in these regions is inherently enhanced due to the cell geometry. This resulted in a distinct separation between the regular nanotubes grown at the center of the samples and the lateral areas, where defective zones appeared. These regions were delineated by elongated opaque lines, shown in Figure 2c, that acted as transition boundaries between stable and unstable growth regimes.



(a) (b) (c)

Figure 2: Delamination issue occurred during the second anodization step on Ti substrate, where part of the oxide layer broke into small pieces under low pressure applied (a). State of an anodized Ti substrate after the system reached the dielectric breakdown limit during electrochemical oxidation (b). Close-up image of a sample showing the dark, gold layer where regular nanotubular structure growth was hindered by the amplification of the local temperature at the lateral zones (c).

Through iterative anodization experiments and confrontation with the existing literature, the electrolyte usage was optimized to achieve the reliable fabrication of free-standing membranes.

3.2. Analysis on photocatalytic performance

The dye concentration during photodegradation tests exhibited a progressive decrease for all investigated samples, confirming the photocatalytic nature of the oxide layer.
By applying the Langmuir-Hinshelwood kinetic model, a linear relationship was obtained by plotting the natural logarithm of the absorbance of the solution normalized to its initial value as a function of irradiation time (Figure 3 and 4). Two graphs are reported below, offering a visual representation of the outcomes of photodegradation tests from anodized Ti substrates and free-standing TiO_2 membranes.

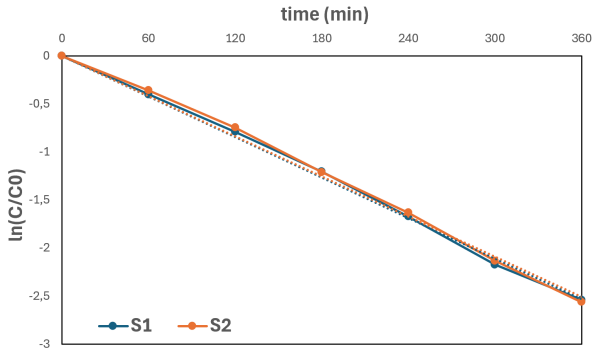


Figure 3: Plot of the Langmuir-Hinshelwood equation and its linear regression for two Ti substrates after single-step anodization in potentiodynamic conditions and thermal annealing.

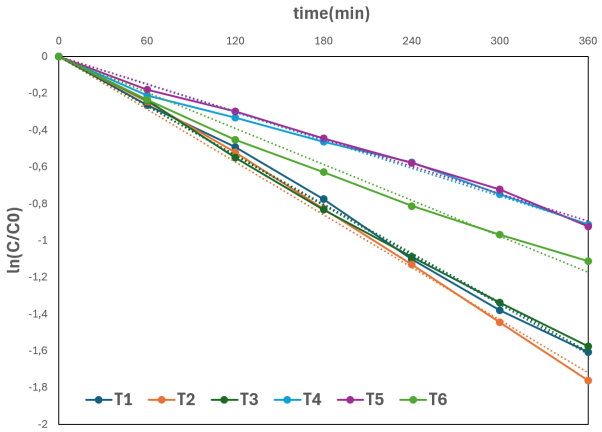


Figure 4: Plot of the Langmuir-Hinshelwood equation and its linear regression for six free-standing membranes synthesized with the standard three-step anodic oxidation process.

When comparing free-standing membranes with anodized titanium substrates, differences in photocatalytic efficiency were observed. Although both configurations exhibited evident photocatalytic activity, the outcomes for the membranes showed slower photodegradation kinetics and more scattered data. This behavior was associated with the reproducibility and quality of the experiments. While for anodized Ti substrate, the oxide layer remained 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. Nonetheless, after evaluating the specific reaction rate constants with respect to the exposed area, the results from both configurations were very similar, as shown in Table 1, highlighting the efficacy of the oxide layer in degrading the organic dye.

Table 1: Table reporting the specific reaction rate constants ($k_{specific}$) for both the two anodized Ti substrates (S), and the six free-standing TiO_2 nanotubular membranes tested (T).

Sample	$\boldsymbol{k}_{\text{specific}}$ [min^{-1} cm^{-2}]
S1	1.56×10^{-3}
S2	1.60×10^{-3}
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}

The encouraging outcomes from these photodegradation experiments constituted a solid baseline for subsequent functionalization of the nanotubes with quantum dots for enhanced photocatalytic activity.

3.3. Assessment on enhanced photocatalysis through quantum dot loading

To evaluate the photocatalytic performance of both free-standing membranes and anodized substrates after quantum dot loading, the same photodegradation procedures previously applied to bare oxide layers were followed. Photodegradation tests performed on free-standing membranes after deposition of $CdSe/CdS$ core-shell and $CdSe$ (core-only) quantum dots yielded the absorbance values of the Rhodamine-B solution. The degradation trend was analyzed through the Langmuir-Hinshelwood model, and the specific reaction rate constants were determined from the linear regression of the resulting curves.
Despite the intrinsic fragility of free-standing nanotubular membranes, which resulted in scattered data and compromised the reliability of the experiment, the evaluation of the specific reaction rate constants, shown in Figure 5, still allowed a comparative assessment.
Compared to core-only quantum dots, quasi-type 1 core-shell heterostructures demonstrated better photocatalytic efficiency, which was attributed to their ability to extend light absorption in the visible range and to promote fast elec-

tron transfer from the $CdSe$ shell to the TiO_2 nanotubes, leading to efficient degradation of the organic dye. As for the optimal loading range of quantum dots identified at the lowest volume employed in this experiment, such as 5 μL, 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.

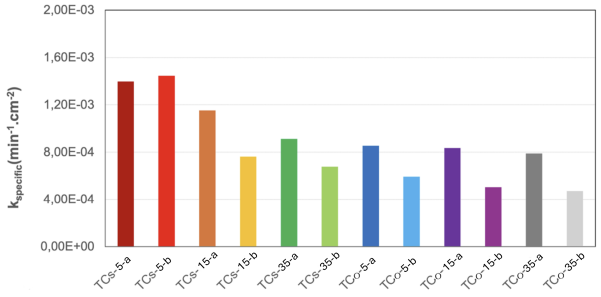


Figure 5: Comparison between the specific reaction rate constants of the first two batches of QD-loading, where core-shell and core-only nanoparticles have been loaded on free-standing membranes.

Significant improvements in the photocatalytic performance were also reported for both core-shell and core-only quantum dot-loaded anodized Ti samples. The curves derived from the Langmuir-Hinshelwood law as a function of irradiation time exhibited steeper slopes after nanotube functionalization, indicating faster photodegradation kinetics.
The specific reaction rate constants obtained from the anodized Ti substrates, before and after functionalization with core-shell and core-only quantum dots, have been reported in Figure 6.

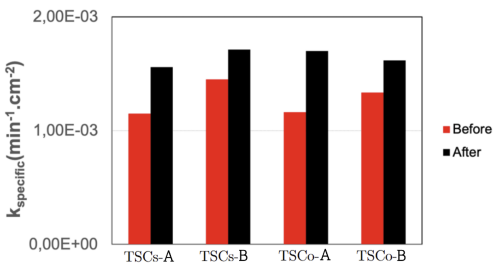


Figure 6: Comparison between the specific reaction rate constants evaluated from photodegradation tests with anodized Ti substrates before and after quantum dot loading.

As illustrated in the graph above, the difference in performance between core-shell and core-only QD loading is less evident compared to the results from loaded free-standing membranes. Interestingly, 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.
As the outcomes of photodegradation tests on functionalized oxide layers exhibited evident discrepancies between samples prepared under identical conditions, further analyses were conducted to assess the capability of the drop-casting technique to produce reproducible data. New anodized substrates were synthesized with a single-step potentiodynamic anodization and functionalized with core–shell and core-only quantum dots at lower loading volumes (0.05, 0.25, 0.5, and 5 μL).
The photocatalysis tests revealed that the highest specific reaction rate constants for both core-shell and core-only systems, reported in Figure 7, were obtained at the lowest loading volume, confirming that excessive nanoparticle deposition can cause nanotube clogging and reduce the photocatalytic performance. However, despite quantum dot loading strongly enhancing the photocatalytic activity, the results highlighted the limited reproducibility of the drop-casting technique. Due to its high sensitivity to deposition parameters, which may lead to non-uniform nanoparticle distribution, further optimization of the loading procedure is required to achieve consistent results.

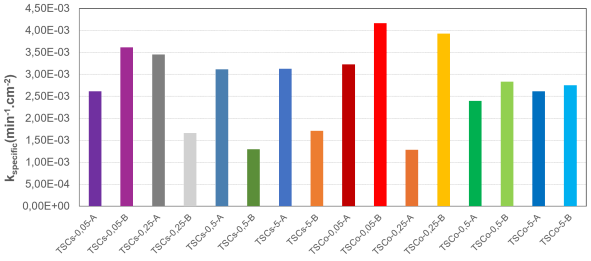


Figure 7: Comparison between the specific reaction rate constants evaluated from photodegradation tests with anodized Ti substrates after core-shell and core-only quantum dot loading.

4. Conclusions

The three-step electrochemical anodization process enabled the fabrication of self-organized nanotubular TiO_2 membranes. However, the process proved to be highly sensitive to the electrolyte conditions. After multiple anodization experiments, the degradation of the solution altered the nanotube growth and affected the structural integrity of the oxide layer. Therefore, careful control and optimization of the electrolyte usage were fundamental for the production of stable and uniform nanotubular membranes.

Despite these limitations, both free-standing membranes and anodized Ti substrates exhibited optimal photocatalytic activity, supporting the reliability of TiO_2 nanotubes in degrading the organic contaminant.

The assessment of quantum dot functionalization demonstrated a clear enhancement of the photodegradation performances, highlighting the effectiveness of this surface modification technique, even with the oxide layer still bonded to the substrate.

Overall, these experimental results demonstrate the critical aspects of the synthesis of TiO_2 nanotubes by electrochemical oxidation, while also showing the viability of the method in producing systems for water purification purposes. Future research should focus on the following points:

- Further investigation on the factors influencing titania nanotube growth during electrochemical anodization.
- Photocatalytic tests conducted on TiO_2 nanotubular membranes loaded 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.

References

[1] Z. Zhu, Y. Xu, Y. Luo, W. Wang, and X. Chen, "Porous evaporators with special wettability for low-grade heat-driven water desalination," *Journal of Materials Chemistry A*, vol. 9, no. 2, pp. 702–726, 2021.

[2] R. Djellabi, L. Noureen, V.-D. Dao, D. Meroni, E. Falletta, D. D. Dionysiou, and C. L. Bianchi, "Recent advances and challenges of emerging solar-driven steam and the contribution of photocatalytic effect," *Chemical Engineering Journal*, vol. 431, p. 134024, 2022.

[3] K. Liu, M. Cao, A. Fujishima, and L. Jiang, "Bio-inspired titanium dioxide materials with special wettability and their applications," *Chemical reviews*, vol. 114, no. 19, pp. 10044–10094, 2014.

[4] Z. Gan, X. Wu, M. Meng, X. Zhu, L. Yang, and P. K. Chu, "Photothermal contribution to enhanced photocatalytic performance of graphene-based nanocomposites," *ACS nano*, vol. 8, no. 9, pp. 9304–9310, 2014.

[5] K. Gulati, R. D. O. Martinez, M. Czerwiński, and M. Michalska-Domańska, "Understanding the influence of electrolyte aging in electrochemical anodization of titanium," *Advances in Colloid and Interface Science*, vol. 302, p. 102615, 2022.