INTREE GRADUATE SCHOOL

PHD CALL
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2025

TITLE :

Tailoring TiO_2 Nanostructures via Oblique Growth for Efficient Photo(electro)catalytic Hydrogen Generation

SUPERVISOR(S)

1ST SUPERVISOR

Name, surname	E-mail adress	HDR
Fabien PAUMIER	fabien.paumier@univ-poitiers.fr	Oui
Pierre Fehlen	pierre.fehlen@univ-poitiers.fr	Non

Laboratory	Position	Team
Pprime	MCF	PPNa

PhD supervision Ratio : 40% F.Paumier, 20% P. Fhelen

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Doctoral student(s) supervised :

Name, surname	Year of doctorate	Percentage of supervision per PhD student

Publication referencing the IntREE program DOI :

2ND SUPERVISOR

Name, surname	E-mail adress	HDR
Dodzi ZIGAH	Dodzi.zigah@univ-poitiers.fr	Oui

Laboratory	Position	Team
IC2MP	Pr	SAMCat

PhD supervision Ratio : 40%

COFUNDING : 0%

KEY WORDS

physical vapor deposition, photoelectrocatalysis, photocatalysis

NATIONAL COLLABORATION

Name, surname	E-mail adress	HDR

Laboratory	Position	Team

Name, surname	E-mail adress	HDR

Laboratory	Position	Team

SUBJECT: 3 PAGES MAX.

1. Scientific Context and Challenges

The urgent need to reduce greenhouse gas emissions and to protect water and air resources has made it essential to develop clean, solar-powered technologies for both energy production and environmental remediation. Among them, photocatalysis and photoelectrocatalysis are particularly promising, as they rely on the direct conversion of solar energy to drive chemical transformations such as water splitting to produce hydrogen, or the oxidative degradation of organic pollutants.

Semiconductors like titanium dioxide (TiO_2) have long been studied for these purposes due to their stability, low cost, and non-toxicity. However, they present major limitations: their wide bandgap (≈3.2 eV) restricts absorption to the UV region of the solar spectrum, while their bulk structure offers limited surface area and promotes fast recombination of photogenerated electron-hole pairs. These issues significantly limit the overall efficiency of photocatalytic and photoelectrocatalytic devices.

To address these bottlenecks, recent advances in nanostructuration offer new paths forward. Oblique Angle Deposition (OAD) is a physical vapor deposition technique that enables the controlled growth of highly porous, anisotropic, and tunable thin films. By adjusting the angle and azimuthal rotation of the substrate, it is possible to create complex architectures such as tilted columns or helicoidal nanostructures (Figure 1). These geometries enhance light scattering, increase the effective surface area, and promote directional charge transport, all of which contribute to improving photocatalytic efficiency.

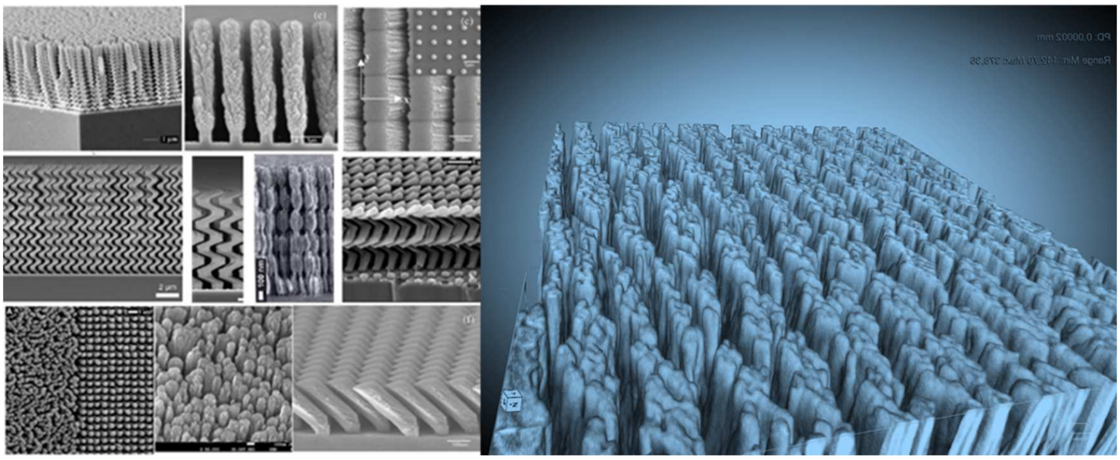

Figure 1 : (left) SEM image, (right) Tomography image of nanostructure obtained by AOD.

Furthermore, the OAD technique allows for the in-situ introduction of dopants (e.g., nitrogen, carbon) or plasmonic nanoparticles (e.g., Au, Ag, Pt), enabling additional functionality. Nitrogen doping can reduce the bandgap and activate the material under visible light. Meanwhile, plasmonic effects, particularly localized surface plasmon resonance (LSPR), induce strong local electromagnetic fields and hot-electron injection, further enhancing the absorption and reactivity of the material.

Combining these approaches provides a unique opportunity to develop advanced TiO_2-based materials for dual-purpose applications: green hydrogen production via photoelectrochemical water splitting, and pollution control through the breakdown of environmental contaminants. The project fits into broader goals of creating multifunctional coatings, including self-cleaning or anti-fouling surfaces, that contribute to sustainable technologies for energy and the environment.

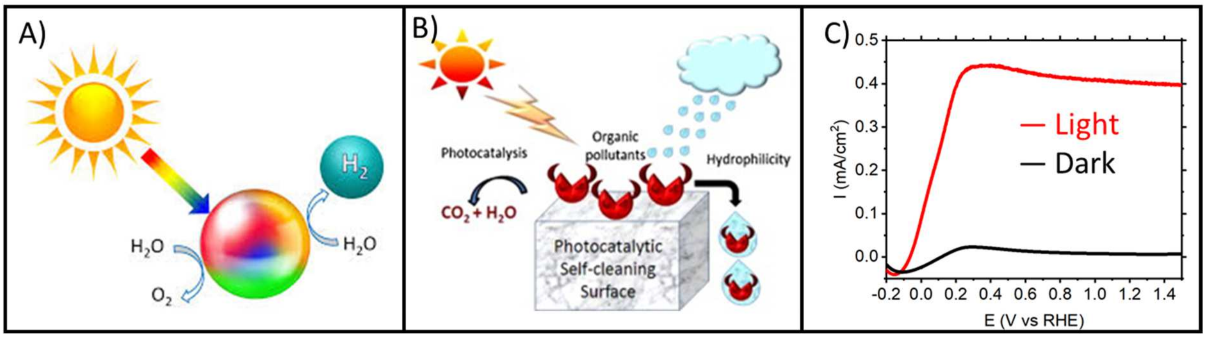

Figure 2: (A) Solar-driven water splitting for hydrogen production on nanoprticules. Under solar illumination, photogenerated electrons and holes participate in the reduction of protons (H^+) to H_2 and oxidation of water to O_2. (B) Photocatalytic self-cleaning surface: upon exposure to sunlight, the photocatalytic surface degrades organic pollutants (e.g., into CO_2 and H_2O), while simultaneously exhibiting increased hydrophilicity, allowing rainwater to remove residues and maintain surface cleanliness. (C) I-E curves, showing the current in dark condition and under illumination using a solar simulator on TiO_2 photoanode

2. PhD Objectives

The main objective of this PhD project is to develop, characterize, and optimize nanostructured TiO_2 thin films grown by OAD, and to investigate their photo(electro)catalytic properties under simulated solar illumination. These materials will be studied both for their ability to degrade organic pollutants via photocatalysis and for their performance in hydrogen production through photoelectrochemical water splitting.

The first goal is to fabricate TiO_2-based thin films with finely controlled morphology, porosity, and crystallinity. The OAD technique offers a high degree of flexibility in designing nanostructured architectures, which will be exploited to maximize light absorption and charge separation. In parallel, the films will be modified through nitrogen doping to enable visible-light activation, and noble metal nanoparticles (such as platinum or gold) will be incorporated to reduce electron-hole recombination and potentially induce plasmonic effects that enhance catalytic efficiency.

A second objective is to build model photoelectrodes based on these materials. This includes the development of TiO_2 photoanodes for water oxidation and the modification of p-type silicon substrates with nickel to serve as efficient photocathodes for water oxidation. These systems will be systematically evaluated using photocatalytic degradation tests and a full suite of photoelectrochemical techniques, including chronoamperometry, cyclic voltammetry, and electrochemical impedance spectroscopy.

Finally, a key part of the project will involve establishing clear relationships between the optical, structural, and chemical properties of the films and their catalytic performance. This will allow the identification of the most promising material configurations and help guide future developments in solar energy conversion and environmental remediation technologies.

3. Methodology and Work Plan

The TiO_2 thin films will be grown at Institut **Pprime** using advanced OAD setups (DIVA and SAFRAN platforms). The nanostructure will be tuned by varying deposition angles, substrate rotation, and process conditions. Doping will be introduced via nitrogen plasma or controlled gas atmospheres, and noble metal nanoparticles will be incorporated by co-deposition or surface flashing followed by thermal annealing. Microstructural and optical characterizations will be performed at **Pprime** using SEM, FIB-tomography, ellipsometry, and spectroscopic techniques. Advanced nanoscale analyses (TEM/STEM, EDX, EELS) will be conducted in collaboration with the University of Seville, leveraging their expertise in electron microscopy. At **IC2MP**, the photoelectrochemical properties of the films will be systematically studied. Techniques will include chronoamperometry, cyclic voltammetry, electrochemical impedance spectroscopy, and hydrogen quantification via gas chromatography. The electrodes will be tested under simulated solar illumination to assess their stability, efficiency, and catalytic behavior. The project also includes the integration of optimized films into multilayer optical architectures (e.g., TiO_2/SiO_2 anti-reflective stacks) and the exploration of their potential for multifunctional applications such as self-cleaning coatings.

4. Candidate Profile

We are looking for a highly motivated candidate with a Master's degree (or equivalent) in materials science, physical chemistry, solid-state physics, or nanoscience. A strong background in one or more of the following areas is desired: thin film deposition, photocatalysis, photoelectrochemistry, surface/interface science, or nanostructured materials. The candidate should demonstrate curiosity, scientific rigor, and the ability to work independently as well as within a multidisciplinary and collaborative research environment. A good command of scientific English (reading and writing) is essential, and experience in experimental lab work will be highly valued.

PUBLICATION ACKNOWLEDGING EUR (DOI)