

Abstract

The habilitation thesis entitled "*Nanostructured Oxides and Conducting Biopolymers: Multifunctional Interfaces for Biomedical, Energy Conversion, Electrochromic and Photoelectrocatalytic Applications*" synthesizes the academic, professional, and scientific achievements accumulated over more than two decades of research and teaching activity at the National University of Science and Technology POLITEHNICA Bucharest, Faculty of Chemical Engineering and Biotechnology.

This work is structured on two complementary research directions, unified by a common methodological framework — synthesis by electrochemical, physical and chemical methods, advanced characterization and functional integration of nanostructured materials — and an applicative vision oriented towards sustainable and biomedical technologies. Direction I addresses nanoscale inorganic oxides (especially TiO_2 , WO_3), and Direction II focuses on systems based on conducting polymers and biopolymers. Together, they define an integrated structure–properties–applications approach, from fundamental electrochemistry to integration into functional devices.

Thus, *research direction I* with the title: "**I.2.1: Multifunctional micro- and nanostructured inorganic oxides for biomedical, photoelectrocatalytic and electrochromic applications**" aims at the controlled fabrication and surface functionalization of TiO_2 and WO_3 nanostructures, respectively, by different methods such as electrochemical anodization, sol–gel method, spin coating, electrospinning and laser texturing. The central objective is the precise control of the morphology, crystallinity and electronic and ionic transport properties, to integrate these nanostructures into hybrid architectures for biomedical implants, HER electrocatalysis, electrochromic smart windows and photocatalytic water decontamination. The four subtopics presented demonstrate a systematic approach, from implant surface engineering to energy conversion and environmental applications.

Subchapter I.2.1.1 refers to the obtaining of TiO_2 nano and micro-structures on the new Romanian alloy Ti6Al7Nb by two methods: electrochemical anodization and laser texturing, systematically investigating the influence of processing parameters on morphology, corrosion resistance and biological response. The original contribution consists in establishing clear correlations between the method of obtaining these structures, the characteristics of the nanostructure and biological performance, providing design criteria for optimized surfaces of titanium-based implants.

Subchapter I.2.1.2 presents Ti/ TiO_2 NTs (NTs-nanotubes) hybrid electrocatalysts decorated with Co or Ag nanoparticles, synthesized by electrochemical reduction and chemical

deposition. These materials exhibit reduced charge transfer resistance, low overpotential and improved Hydrogen Evolution Reaction (HER) activity. A key contribution is the development of TiO₂NTs–metal hybrid nanostructures with improved catalytic efficiency for the production of hydrogen.

Subchapter I.2.1.3 describes the preparation of highly crystalline electrochromic thin films based on WO₃/TiO₂ and TiO₂–PEG (polyethylene glycol) on fluorine doped tin oxide (FTO) substrates, by sol–gel, spin coating, electrospinning and electrochemical deposition methods. Superior electrochromic performances were highlighted by establishing correlations between morphology, charge transport and optical modulation. The novelty lies in synthesizing hybrid nanocomposites with controlled electrochromic characteristics for energy-efficient smart windows.

Subchapter I.2.1.4 discusses a green approach to functionalizing TiO₂ nanotubes with natural molecules — such as polydopamine, silk fibroin-derived carbon quantum dots and chlorophyll — thus obtaining photocatalytic systems active under both UV and visible irradiation, with superior performances in the degradation of organic pollutants in wastewater. This work uniquely demonstrates the development of bio-functionalized TiO₂ hybrid structures, based on the dual S-scheme heterojunction mechanism, for efficient and environmental remediation.

Through this first direction approached, the systematic control of the morphology and surface properties of nanostructures is pursued, integrating inorganic oxides with metals, conducting polymers and bio-inspired molecules, and establishing rigorous structure–property–application correlations with impact in biomedical, energy, environmental and electrochromic technologies.

Research Direction II — "**I.2.2: Development of conducting polymer films and functional membranes based on biopolymers for biomedical, energy and electrochromic applications**" addresses the molecular and nanoscale engineering of functional polymer materials, demonstrating how conducting polymers and biopolymers — integrated with nanostructured oxide surfaces — generate systems with controllable electrical, electrochemical and ionic properties. Complementing the oxide-based strategies of Research Direction I, this direction explores three interconnected areas: **1.** biomedical coatings based on electrodeposited polypyrrole (PPy) on implants, **2.** hybrid polymer–oxide architectures for energy conversion and **3.** bio-inspired solid polymer electrolytes for electrochromic devices. The common principle is the engineering of the polymer substrate and polymer electrolyte interfaces to optimize functional performance.

In subchapter I.2.2.1, the electrodeposition of PPy coatings on Ti6Al7Nb alloy is investigated, rigorously evaluating the effects of synthesis parameters, doping with different surfactants and micro/nano-structuring on the adhesion of the film to the substrate, corrosion resistance and cell viability. The original contribution consists in establishing structure–properties–biological response correlations for optimizing the biocompatibility of implants.

Subchapter I.2.2.2 presents the obtaining of counter-electrodes by integrating poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) films on TiO₂ nanotubes used in natural dye-sensitized solar cells (DSSC). The film morphology, conductivity and interface quality are correlated with the charge transport efficiency and device performance. The novelty lies in the design of polymer–oxide hybrid architectures that maximize electron transfer and energy conversion efficiency.

Subchapter I.2.2.3 describes the synthesis of solid polymer electrolytes based on biopolymers and chromophore-doped deoxyribonucleic acid (DNA), used for the assembly of smart window electrochromic devices. The influence of membrane composition, ionic conductivity and structural organization on the electrochemical stability and device performance was systematically investigated. The novelty consists in the development of bio-inspired electrolyte membranes with enhanced ionic conductivity, good switching kinetics and improved long-term stability.

Together, the two research directions define an original and integrated approach, combining nanoscale inorganic oxides with conducting polymers and biopolymers to create multifunctional systems with controllable morphology, surface properties and performance. The set of contributions advances the fundamental understanding of structure–properties–applications relationships and aligns the work with current international priorities in the field of sustainable, multifunctional and bio-inspired nanomaterials, with demonstrated relevance for both the scientific and industrial communities.