UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL OF CHEMISTRY

PhD THESIS SUMMARY

Ph. D. Student:
Florin Andrei

Supervisor:
Prof. dr. habil. Ioan-Cezar Marcu

2025

PEROVSKITE-BASED MATERIALS FOR PHOTOCATALYTIC APPLICATIONS

The PhD thesis „PEROVSKITE-BASED MATERIALS FOR PHOTOCATALYTIC APPLICATIONS" is focused on the preparation, charaterization, and photocatalytic and photoelectrocatalytic evaluation of complex perovskite-based thin films prepared by pulsed laser depositon (PLD).

Photocatalysis and photoelectrocatalysis are considered the key methods to solving energy generation and environmental pollution problems. They can use the sunlight, which is one of the cleanest and renewable energy sources. Perovskite materials are excellent candidates for these applications due to their high catalytic activities and superior stability. Among them, bismuth ferrite $BiFeO_3$ (BFO) is a multiferroic material with a perovskite-type structure, being among the most studied oxides in this application area due to its excellent chemical stability, strong ferroelectricity and favorable absorption properties (ca. 2.7 eV) compared to other ferroelectric perovskites. Similarly, $LaFeO_3$ (LFO) is a material belonging to the same class of perovskite materials having an optical band gap of ca. 2.07 eV, with the absorption capacity mainly in the visible region of the spectrum and it receives considerable attention due to its strong photo- and photoelectro- catalytic activities. Due to their major advantages, they formed the basis of the study in this PhD thesis.

The thesis is structured in two major parts, one related to the theoretical concepts involved and studied in this thesis coupled with a wide view of the state of the art in the photo- and photoelectro- catalytic application of perovskites, and the other composed by original experimental results, each of them being divided into several chapters.

In the first chapter, a general view related to the chemical composition, structure and properties of inorganic perovskite materials are presented. Photocatalytic applications of perovskite materials are the main goal of this thesis, as pointed out in the title. The purpose of the last part of chapter 1 is to highlight the state of the art concerning the influence of the physico-chemical properties of perovskite-type materials on their photo- and photoelectro- catalytic efficiencies, focusing mainly on the production of H_2 and O_2 via water splitting reaction.

The second chapter reveals the theoretical aspects related to the thin films preparation method, their characterization techniques and evaluation of their applications. The theoretical principle of laser-based techniques (e.g. PLD) with the experimental setup used for thin films preparations followed by the characterization techniques utilized to study the morphological, optical and structural properties of prepared thin films are described here. The chapter ends with the presentation of the photo- and photoelectro- catalytic mechanisms, and the theoretical concepts and the experimental setup used during all studies presented in the thesis.

The experimental part focuses on the preparation, characterization and evaluation of photocatalytic and photoelectrochemical properties of BFO and LFO thin films prepared by pulsed laser deposition technique. The third chapter reveals a detailed study related to the influence of the deposition oxygen pressure on the physico-chemical properties of LFO films grown on highly oriented Nb-doped $SrTiO_3$ (STON) substrate. Different partial pressures ($6.5x10^{-5}$ up to 0.9 mbar) are used during the preparation of LFO films by PLD. The obtained films are characterized from the morphological, structural and optical points of view. Finally, photoelectrochemical water decomposition reactions were studied in the presence of LFO thin films. According to the high-resolution X-ray diffraction (HR-XRD) patterns, all the LFO/STON films deposited at different oxygen partial pressures are heteroepitaxial, only (00*l*) reflections being observed. Indeed, the oxygen partial pressures used during the deposition processes strongly influences the physicochemical properties of the resulting films. The oxygen vacancies in the prepared thin films are closely related to the experimental conditions. It was found that at 0.6 mbar O_2, the resulting LFO films exhibited an optimal level of oxygen vacancies, leading to the highest photoelectrochemical activity.

The fourth chapter presents a detailed study related to the influence of films' thickness on the photoelectrochemical water-splitting reaction. Thin films are differently growing depending on collector substrates. The covering mechanism, the surface morphology, as well as the physicochemical properties of the thin films are strongly affected by the nature of the substrate and, for a given substrate, by different factors. These aspects are detailed in this chapter, where BFO and LFO films with different thicknesses were grown on conductive STON substrates, whose morphological, structural and optical properties are analyzed. Heteroepitaxial BFO films having thicknesses between 15 and 209 nm are obtained during this study. It is very clear that for thicker samples, the structural strain is reduced, but it is still present even at thicknesses higher than 200 nm. Also, heteroepitaxial films are obtained for LFO, with thicknesses ranging from 14 to 200 nm. The photoelectrochemical properties of these films are studied and their photoelectrocatalytic behavior is in detail analyzed. In the case of BFO films, the highest photocurrent was obtained for the sample having a thickness of 24 nm, the one that showed the highest optical absorption at the used irradiation source. For LFO thin films, the appearance of self-assembled nanopyramid-like structures, along with significant changes in cation Fe/La ratio and implicitly in the functional photoeletrochemical properties is evidenced. Different structural features have been noticed for LFO/STON thin films, from a single orientation - LFO(110)//STO(100) to a double orientation consisting of self-assembled nanopyramids - LFO(001)//STO(100) embedded into a LFO(110)//STO(100) matrix. From the photoelectrochemical measurements performed on LFO/STON with thicknesses above 32 nm, the anodic photocurrent has higher values toward the positive potential, while for the thinnest LFO/STON samples, both photocathodic and photoanodic photocurrents are measured. A direct evaluation of the photocatalytic LFO thin films water splitting efficiency, unbiased hydrogen production performance measurements was also presented in this chapter.

The fifth chapter presents the preparation of a new type of heterostructures based on BFO and LFO thin films and their physicochemical characterization. The influence of films' thickness, as well as heterostructures' architecture on the photoelectrochemical water splitting efficiencies, are important aspects outlined here. The physicochemical properties of the resulting heterostructures are strongly influenced by the experimental conditions used during the PLD process. The obtained results are excellent, the photoelectrochemical properties of LFO/BFO/STON films are improved compared to single BFO and LFO layers deposited on STON, with a maximum photocurrent density of ca. 2.8 mA/cm^2. The film rapidly responds in the presence of light, with no photocurrent spikes that can be associated with the fast recombination of the free charge carriers. The combined effects of imposing structural strain and ferroelectric spontaneous polarization coming from the bottom (BFO) layer over the photoelectrochemical properties of LFO thin films for very thin heterostructures are presented in the final part of this chapter. The LFO/BFO/STON heterostructure exhibits both photocathodic and photoanodic behavior, as well as piezo force microscopy (PFM) domain switching characteristics at relatively low applied dc bias. On the other hand, the BFO/LFO/STON heterostructure barely responded to much higher applied dc field in PFM investigations, accompanied by predominant photoanodic photoelectrochemical behavior. For this BFO-top heterostructure a predominant polarization orientation, characteristic for long-range ferroelectric order with robust single-oriented domains is observed. In contrast, the cooperative effects of competing surface chemistry and polarization of the LFO/BFO interface over the polarization orientation and magnitude is observed for the LFO/BFO/STON heterostructure. The behavior is completely different in photocatalytic reactions, when no external bias is applied. This is because the long-range ferroelectric order is maintained, and the polarization aligns uniformly toward the substrate in heterostructures with BFO as the surface material. This strong alignment in a single direction more efficiently separates photogenerated charge carriers, thereby improving the overall activity of the photochemical reaction. In contrast, for architectures involving LFO as the surface material, the polarization is randomly oriented. This increases recombination during the photocatalytic process and limits hydrogen production.