1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan)

1.1. Project goals

The main aim of the Project's research work is the development and dissemination of innovative strategies for synthesizing nitride-based catalysts for effective "green hydrogen" production. The proposed detailed aims will be based on the synthesis and characterization of nitrides including metal or non-metal nitrides and their composites with oxides, elemental doping, and electrochemical tests. Two main reactions, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) will be the basis of verifying practical application.

1.2. Outline

The key innovation lies in the synthesis of new composite catalysts and controlling the physicochemical and electrochemical properties. A very important element of the ongoing research will be the obtaining of catalysts that are highly stable and bi-functional, i.e., that exhibit activity in both the HER reaction and the OER reaction. Furthermore, the synthesis strategy will be established taking into account the high variability of metals and dopants. The chemical state of atoms will be examined and characterized in order to make possible the choice of the most effective catalysts for the OER and HER reactions. This way, we will gain a precise determination of catalyst site types, which will be particularly important for the interpretation of electrochemical measurements. An important step will be determining the relationship between elemental composition and the materials' electrochemical activity in water splitting in contact with different electrolytes.

1.3. Work plan

The Project will be developed through four scientific work packages (WP1-WP4) described in detail below.

WP1: Synthesis of nitrides by various methods

The main objectives of WP1 are to obtain catalysts for effective water splitting (WP4). As part of WP1, metal and non-metal Ns will be synthesized using different procedures: (1) using hydrothermal process, or (2) heating at tube furnace in NH_3, argon or nitrogen atmosphere. Additionally, to obtain catalysts; elemental-doped Ns will be synthesized to regulate the adsorption, electronic, and physicochemical properties. Elemental doping will be the incorporation of heteroatoms or impurities (metal or non-metal elements). Planned research includes: (1) preparation of Ns doped with metals, (2) preparation of Ns doped with non-metals. Transition metals, e.g., cobalt, manganese, iron, nickel, or their derivatives are very promising for water electrolysis due to their unique d electronic structure and abundant reserves, and therefore will be introduced to catalysts'. To regulate adsorption, and electronic, physicochemical properties, heteroatoms, e.g., nitrogen, phosphorus, sulphur, and boron will be introduced to the structure. It is also possible to introduce metal oxides depending on the given materials' properties.

WP2: Synthesis of hybrid materials containing nitrides and carbon matrix

To improve the metal and non-metal Ns properties, such as dispersion of active sites, and to prevent the catalysts from aggregating, the hybrids will be manufactured with carbon matrix with various properties.

A carbon matrix almost automatically provides two key features, i.e., chemical stability and a high electric conductivity.

WP3: Physicochemical characterization of the obtained nanostructured catalysts

A set of laboratory analyses of samples will be carried out using methods for quantifying heteroatoms, metals (metal oxides), and Ns associated with the carbon. The results of physicochemical analyses will be integrated within the samples' properties and certain parameters, like elemental composition, will be analysed using different methods, such as elemental combustion analysis, Raman spectroscopy, XDR, EDX, and XPS, to determine composition both in the bulk and on the surface. This way, we will make a precise determination of the type of catalyst places, which is particularly important for later WP4 electrochemical measurement interpretation. The materials' structure will be studied by means of electron microscopy SEM, HRTEM, and the method of low-temperature nitrogen adsorption.

WP4: Electrochemical investigations – oxygen evolution reaction and hydrogen evolution reaction

The electrochemical tests of the samples obtained in WP1 and WP2, undertaken to prove the newly obtained materials' practical applicability in water splitting, i.e., whether they are active in HER and OER. Studies of electrochemical activity regarding the Ns and their hybrids will be carried out. The materials selected will be analysed as catalysts for water splitting.

1.4. Literature

[1] J. Joy, J. Mathew, S.C. George, Nanomaterials for photoelectrochemical water splitting–review, International Journal of Hydrogen Energy 43(10) (2018) 4804-4817.
[2] J. Zhang, Q. Zhang, X. Feng, Support and interface effects in water-splitting electrocatalysts, Advanced Materials 31(31) (2019) 1808167.
[3] T. Yao, X. An, H. Han, J.Q. Chen, C. Li, Photoelectrocatalytic materials for solar water splitting, Advanced Energy Materials 8(21) (2018) 1800210.
[4] L. Lin, Z. Yu, X. Wang, Crystalline carbon nitride semiconductors for photocatalytic water splitting, Angewandte Chemie 131(19) (2019) 6225-6236.
[5] Y. He, T. Hamann, D. Wang, Thin film photoelectrodes for solar water splitting, Chemical Society Reviews 48(7) (2019) 2182-2215.
[6] Y. Guo, T. Park, J.W. Yi, J. Henzie, J. Kim, Z. Wang, B. Jiang, Y. Bando, Y. Sugahara, J. Tang, Nanoarchitectonics for transition-metal-sulfide-based electrocatalysts for water splitting, Advanced Materials 31(17) (2019) 1807134.
[7] Y. Sun, T. Zhang, C. Li, K. Xu, Y. Li, Compositional engineering of sulfides, phosphides, carbides, nitrides, oxides, and hydroxides for water splitting, Journal of Materials Chemistry A 8(27) (2020) 13415-13436.
[8] M.B. Zakaria, D. Zheng, U.-P. Apfel, T. Nagata, E.-R.S. Kenawy, J. Lin, Dual-Heteroatom-Doped Reduced Graphene Oxide Sheets Conjoined CoNi-Based Carbide and Sulfide Nanoparticles for Efficient Oxygen Evolution Reaction, ACS applied materials & interfaces 12(36) (2020) 40186-40193.
[9] R. Paul, M. Wang, A. Roy, Transparent Graphene/BN-Graphene Stacked Nanofilms for Electrocatalytic Oxygen Evolution, ACS Applied Nano Materials (2020).
[10] S. Kundu, K. Bramhaiah, S. Bhattacharyya, Carbon-based nanomaterials: in the quest of alternative metal-free photocatalysts for solar water splitting, Nanoscale Advances (2020).

1.5. Required initial knowledge and skills of the PhD candidate

1) Basic knowledge in the area of electrode materials and design
2) Basic knowledge in the area of materials characterization methods
3) Ease of learning and accepting new knowledge
4) Innovative attitude to problem solving
5) Knowledge of carbon material science
6) Good knowledge of English with particular emphasis on scientific language

1.6. Expected development of the PhD candidate's knowledge and skills

1) Electrode materials design
2) Methods for water molecule split
3) Analytical thinking
4) Cooperation spirit and team work ability
5) R&D project management
6) Writing of grant applications and research papers
7) Results and projects presentation at conferences
8) Communication in English