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

Project title: Transition metal nitrides doped with heteroatoms as highly stable catalysts for green hydrogen production

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 transition metal nitrides, 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 bifunctional, 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 (Co, Ni, Mo) and dopants (N, S). 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 metal nitrides MNs (M=Co, Ni, Mo) by various methods.

In WP1 metal (cobalt, nickel, molybdenum) nitrides will be synthesized using following methods:

1. Using hydrothermal process (max. temperature up to 250°C).
2. Heating at tube furnace in Ar, N_2, or NH_3 atmosphere (max. temperature up to 1000°C with the heating range between 1 and 10°C/min).

WP2: Synthesis of hybrid materials containing metal nitrides and carbon matrices doped with non-metallic heteroatoms (N, S).

Hybrid materials containing metal nitrides and carbon matrices doped with non-metallic heteroatoms (N, S) will be introduce to improve the nitrides properties in particular provide better conductivity, a larger surface area, prevent aggregation effects and ensure good dispersion of active centres.

WP3: Characteristics of physicochemical properties of the obtained materials

The project will carry out a thorough study of the physicochemical properties of the obtained hybrid

electrocathalysts using instrumental techniques such as:

- scanning electron microscope (SEM) with the energy-dispersive X-ray spectrometer (EDX);
- transmission electron microscope (TEM);
- X-ray diffraction (XRD);
- X-ray photoelectron spectroscopy (XPS);
- Raman spectroscopy;
- elemental analysis;
- sorption of nitrogen analysis.

WP4: Electrochemical characterization

The obtained materials will be electrochemically characterized to evaluate their activity towards water splitting reactions, including the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). The following techniques will be used:

- Linear Sweep Voltammetry (LSV);
- Cyclic Voltammetry (CV);
- Electrochemical Impedance Spectroscopy (EIS);
- Chronopotentiometry (CP).

1.4. Literature

[1] X. Gao, Y. Chen, Y. Wang, L. Zhao, X. Zhao, J. Du, et al., Next-generation green hydrogen: progress and perspective from electricity, catalyst to electrolyte in electrocatalytic water splitting, Nano-Micro Letters, vol. 16, p. 237, 2024.

[2] S. A. Kadam, L. M. Jose, N. S. George, S. Sreehari, D. Nayana, D. Van Pham*, et al.*, Recent progress in transition metal nitride electrodes for supercapacitor, water splitting, and battery applications, *Journal of Alloys and Compounds,* vol. 976, p. 173083, 2024.

[3] H. S. Gujral, G. Singh, A. V. Baskar, X. Guan, X. Geng, A. V. Kotkondawar*, et al.*, Metal nitride-based nanostructures for electrochemical and photocatalytic hydrogen production, *Science and Technology of Advanced Materials,* vol. 23, pp. 76-119, 2022.

[4] H. Guo, A. Wu, Y. Xie, H. Yan, D. Wang, L. Wang*, et al.*, 2D porous molybdenum nitride/cobalt nitride heterojunction nanosheets with interfacial electron redistribution for effective electrocatalytic overall water splitting, *Journal of Materials Chemistry A,* vol. 9, pp. 8620-8629, 2021.

[5] L. Yu, S. Song, B. McElhenny, F. Ding, D. Luo, Y. Yu*, et al.*, A universal synthesis strategy to make metal nitride electrocatalysts for hydrogen evolution reaction, *Journal of Materials Chemistry A,* vol. 7, pp. 19728-19732, 2019.

[6] C. Huang, J. Zhou, D. Duan, Q. Zhou, J. Wang, B. Peng, et al., Roles of heteroatoms in electrocatalysts for alkaline water splitting: A review focusing on the reaction mechanism, Chinese Journal of Catalysis, vol. 43, pp. 2091-2110, 2022.

[7] J. Wang, T. Liao, Z. Wei, J. Sun, J. Guo, and Z. Sun, Heteroatom-doping of non-noble metal-based catalysts for electrocatalytic hydrogen evolution: an electronic structure tuning strategy, *Small Methods,* vol. 5, p. 2000988, 2021.

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