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

Project title: Innovative graphene-based catalysts for water splitting technology as "green" method for hydrogen production

1.1. Project goals

- ✓ The Project and its outcomes' target is an important contribution to solving a worldwide environmental issue of energy storage.
- ✓ The Project's aim is the synthesis of effective water splitting electrode materials and practical verification of their application-oriented features.
- ✓ Co-operation with the research group of the Supervisor will strengthen the knowledge and skills in the area of contemporary and future trends in the design of electrode materials for electrochemical energy devices.

1.2 Outline

The Project and its outcomes' target is an important contribution to solving a worldwide environmental issue. Efficient electrolysis of water is commonly seen as a way to accumulate the excess energy that may be produced by some renewable sources, as photovoltaics. This excess could power the electrolysis process, which yields hydrogen, i.e., the fuel with the highest energy density per volume unit. This concept is in line with hydrogen economy perspectives. The crucial element for water electrolysis is an efficient electrode design which enables a low split potential alongside high durability. The Project's aim is the synthesis of such electrode materials and practical verification of their application-oriented features. The main objectives are to obtain catalysts, i.e., 3D-structured graphene enriched with heteroatoms, metal oxides, perovskite metal oxides, transition metal sulfides, nitrides or carbides. The catalysts most promising from the perspective of water splitting will be discerned and described in detail on the basis of physical and chemical analyses. The synthesis strategy will be established considering the high variability of metal oxides, heteroatom dopants, perovskite metal oxides, transition metal sulfides, nitrides or carbides. The chemical state of atoms will be examined and characterized to make it possible to choose the most effective catalysts for the oxygen evolution reaction and hydrogen evolution reaction. This way, we will gain a precise determination of catalyst site types, which will be particularly important for the interpretation of electrochemical measurements. Important step is determine the relationship of morphology and elemental composition with the materials' electrochemical and photoelectrochemical (water splitting) activity, as well as their hydrogen evolution reaction activity in contact with aqueous electrolytes.

1.3. Work Plan:

1. <u>Graphene selection:</u> employing previous studies by Project supervisor and mentor as well as open access databases and publications in order to choose the most effective synthesis method.

2. <u>Preparation of 3D structured graphene using:</u>

a) Hard-templating (e.g., Ni-foam, SiO_2, $CaCO_3$, K_2CO_3, Na_2CO_3), then using thermal treatment (in an inert gas atmosphere, at a carbonization temperature dependent on the type of template) and removing templates from the structure;

b) Soft-templating (organic template, polymers, e.g., polyurethane foam), then using thermal treatment (in an inert gas atmosphere, at a carbonization temperature dependent on the type of template) and optionally removing template residues;

c) Stabilizing graphene into a 3D graphene structure with selected heteroatom-containing reagents (e.g., chitosan, gelatine, green algae, amino acids, chitin, polyaniline, polyacrylonitrile).

The process of stabilization will be guided in lyophilisator. The solvent will be removed during a low temperature dehydration process in the lyophilisator under reduced temperature and pressure. After this, the 3D-structure of graphene with the heteroatom precursor will be carbonized to obtain graphene hybrid materials containing heteroatom functional groups appropriate for electrochemical applications.

<u>3. Preparation of 3D-structured graphene with heteroatoms, metal oxides, perovskite-type metal oxides, transition metal sulfides, nitrides or carbides:</u>
Depending on the 3D structurization of graphene (hard/soft templating method or stabilized in lyophilisator), to improve their electrochemical properties it is important to obtain:
a) Hybrids of graphene with nitrogen, boron, phosphorus, or sulphides, as well as dual- or three-doping heteroatoms. The following are examples proposed for use in synthesis: H_3BO_3, urea, BCl_3, polyaniline, polypyrrole, H_3PO_4, thiourea;
b) Hybrids of graphene with metal oxides (based on e.g., Mo, Co, Ce, La, Mn, Sr, Ba, Pr, Fe), perovskite-type metal oxides (containing, e.g., lanthanides), transition metal sulfides, transition metal nitrides, and transition metal carbides.

<u>4. Graphene structure analysis:</u> material structure will be studied using Raman spectra interpretation, nitrogen sorption analysis, and structure description based on scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images. Primary adsorption data will be regressed according to certain theoretical models such as the Brunauer-Emmett-Teller (BET) theory, Horvath-Kawazoe (HK), and non-local density functional theory (NLDFT).

<u>5. Analysis of elemental composition:</u> elemental combustion analysis, energy dispersive X-ray analysis (EDX), X-ray diffraction analysis (XRD), and X-ray photoelectron spectroscopy analysis (XPS) of metal oxides, perovskite metal oxides, transition metal sulfides, nitrides or carbides and non-metal heteroatom content in samples to determine composition both in the bulk and on the surface. This way, we will gain a precise determination of catalyst site types, which will be particularly important for the interpretation of electrochemical measurements.

Deliverables:
1. Description of the synthesis of graphene-based enriched with selected non-metal heteroatoms.
2. Description of the synthesis of graphene enriched with selected metal oxides, perovskite-type oxides, transition metal sulfides, nitrides or carbides.
3. Description of physical and chemical properties of graphene-based samples.
4. A series of publication in top ranked journals of high impact.

1.4. Literature

[1] I. Dincer, Green methods for hydrogen production, International journal of hydrogen energy 37(2) (2012) 1954-1971.
[2] J. Joy, J. Mathew, S.C. George, Nanomaterials for photoelectrochemical water splitting–review, international journal of hydrogen energy 43(10) (2018) 4804-4817.

[3] J. Zhang, Q. Zhang, X. Feng, Support and interface effects in water-splitting electrocatalysts, Advanced Materials 31(31) (2019) 1808167.
[4] T. Yao, X. An, H. Han, J.Q. Chen, C. Li, Photoelectrocatalytic materials for solar water splitting, Advanced Energy Materials 8(21) (2018) 1800210.
[5] L. Lin, Z. Yu, X. Wang, Crystalline carbon nitride semiconductors for photocatalytic water splitting, Angewandte Chemie 131(19) (2019) 6225-6236.
[6] Y. He, T. Hamann, D. Wang, Thin film photoelectrodes for solar water splitting, Chemical Society Reviews 48(7) (2019) 2182-2215.
[7] 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.
[8] 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.
[9] 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.
[10] R. Paul, M. Wang, A. Roy, Transparent Graphene/BN-Graphene Stacked Nanofilms for Electrocatalytic Oxygen Evolution, ACS Applied Nano Materials (2020).
[11] P. Bhanja, Y. Kim, B. Paul, Y.V. Kaneti, A.A. Alothman, A. Bhaumik, Y. Yamauchi, Microporous nickel phosphonate derived heteroatom doped nickel oxide and nickel phosphide: Efficient electrocatalysts for oxygen evolution reaction, Chemical Engineering Journal 405 (2021) 126803.
[12] 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) Basic 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