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

Project title: The conversion of CO_2 into high-value chemicals – design of highly active catalysts, based on new carbon-MOF composites

1.1. Project goals

The main objective of the project is the design of highly active, novel catalysts for CO_2 conversion into hydrocarbons, alcohols, acids, and other high-value products. The main question to answer is whether or not MOF@carbon nanocomposites can work as active and stable catalysts under non-thermal plasma conditions. We would also like to explore the role of nitrogen incorporated into the carbon matrix and the role of porosity on catalytic efficiency.

The particular goals:

- Synthesis and full physicochemical characterization of MOF@C composites using adsorptive and spectroscopic techniques
- Non-thermal plasma (NTP) parameters investigations
- Tackling Climate Change, our duty is to contribute to lowering greenhouse gas emissions and delaying climate change.
- Energy Security: It can help improve energy security by reducing reliance on imported fossil fuels.
- Job Creation: Jobs can be created by developing and implementing sustainable fuel and chemical production technologies.
- Economic Growth: It can open up new business opportunities and promote economic expansion.
- Environmental advantages: The proposed study can support the advancement of environmentally friendly business practices and lessen the environmental impact of diverse businesses.

1.2. Outline

There is a growing portfolio of carbon dioxide removal technologies, including those inspired by nature. The carbon dioxide removal solutions have the potential to serve as a necessary defense against pending climate catastrophe. One of the main difficulties is in the **stability and relative inertness of CO_2**, which makes its reduction quite challenging. The majority of conversion and removal methods rely on high-energy usage, i.e. high-temperature and/or high-pressure conditions. On the other hand, CO_2 reduction under NTP environment occurs under relatively mild conditions with a lower energy input. The use of NPT has a particular advantage, as it relies on an ON/OFF continuous and readily available power supply. In addition, besides reducing CO_2 emissions into

the atmosphere, photocatalytic methods can also provide high-value chemicals that make such approaches an appealing option to conventional CO_2 removal methods.
The focus of the proposed research is to synthesize the nanocomposite based on Fe or Mn-containing porphyrin paddle-wheel framework supported on an N-doped carbonaceous matrix. To the best of our knowledge THERE ARE NO literature reports on such catalytic systems. Manganese (or iron) containing MOFs due to their stability in various oxidation stages are known as excellent catalysts. On the other hand, the incorporation of nitrogen into the carbon lattice will increase the surface-CO_2 concentration drastically which in turn is expected to rise the catalytic efficiency of CO_2 conversion.

1.3. Work plan

1. **Synthesis of MOFs structures.** TCPP (Tetra(4-carboxyphenyl) porphyrin) based MOF structures will be performed under the solvothermal conditions. The major advantage of this method is good yield of the process and homogeneity of the samples.
2. **Carbon-matrices synthesis. (i) amorphous carbon films, (ii) Graphene oxide, (iii) reduced graphene oxide,**
3. **Nitrogen-doping.** Various amount of doped nitrogen will be introduced to carbon materials to investigate its effects on the catalytic efficiency.
4. **Nanocomposites synthesis.** The hybrids of the obtained MOFs deposited on carbons will be synthesized.
5. **Porosity measurements.** The low-temperature nitrogen adsorption measurements: surface area and volume; H_2O, NH_3, CO_2 will also be used as adsorbate to characterize the material.
6. **Full phys-chem characterization;** all available techniques will be used:
   - SEM/EDS: the size, shape, surface texture and morphology of the crystals, and chemical composition;
   - HRTEM/EDX: the pore size, internal structure and morphology of crystals, helps to analyze the chemical composition of materials;
   - TG: thermal stability of prepared nanomaterials; this technique is a good method to check whether the MOF has been sufficiently activated (no residual solvent molecules);
   - PXRD: the crystal structure, phase composition;
   - Sorption of NH_3, CO_2 and H_2O combined with spectral studies - determination of chemical properties and mechanism of splitting; for the in situ IR study the pelletized samples will be exposed to target gas.
   - Additionally, the obtained materials will be fully characterized spectroscopically: XPS, IR, RS.
7. **Finally, the catalytic process of CO_2 reduction under NPT** (dry or with H_2O) will be evaluated. The collected results will be enriched by in-situ FTIR measurements.

8. The results are expected to be published in high-impact-factor scientific journal.

1.4. Literature *(max. 10 listed, as a suggestion for a PhD candidate)*

1. *Wiśniewski, M., Liu, X., In situ FTIR study of 2D-carbon materials for CO2 splitting under non-thermal plasma environment – selective CO production, Journal of Materials Chemistry A, 2023, DOI: 10.1039/d3ta00953j*
2. *Moszczyńska, J., Liu, X., Wiśniewski, M., Non-Thermal Ammonia Decomposition for Hydrogen Production over Carbon Films under Low-Temperature Plasma—In-Situ FTIR Studies, International Journal of Molecular Sciences, 2022, 23(17), 9638*
3. *Wiśniewski, M., Terzyk, A.P., Non-thermal plasma-assisted catalytic CO_2 conversion over Zn-TCPP 2D catalyst, Adsorption, 2020, 26(7), pp. 1165–1171*
4. *Wiśniewski, M., Bieniek, A., Bolibok, P., ...Kowalczyk, P., Terzyk, A.P., Mechanistic aspects of water adsorption-desorption in porphyrin containing MOFs, Microporous and Mesoporous Materials, 2019, 290, 109649*
5. *Wiśniewski, M., Koter, S., Terzyk, A.P., Włoch, J., Kowalczyk, P., CO_2 - Reinforced nanoporous carbon potential energy field during CO_2/CH_4 mixture adsorption. A comprehensive volumetric, in-situ IR, and thermodynamic insight, Carbon, 2017, 122, pp. 185–193*
6. *Xu, S., Chansai, S., Shao, Y., ...Fan, X., Hardacre, C., Mechanistic study of non-thermal plasma assisted CO_2 hydrogenation over Ru supported on MgAl layered double hydroxide, Applied Catalysis B: Environmental, 2020, 268, 118752*
7. *Chen, H., Mu, Y., Xu, S., ...Hardacre, C., Fan, X., Recent advances in non-thermal plasma (NTP) catalysis towards C1 chemistry, Chinese Journal of Chemical Engineering, 2020, 28(8), pp. 2010–2021*
8. *Xu, S., Chansai, S., Xu, S., ...Hardacre, C., Fan, X., CO Poisoning of Ru Catalysts in CO_2Hydrogenation under Thermal and Plasma Conditions: A Combined Kinetic and Diffuse Reflectance Infrared Fourier Transform Spectroscopy-Mass Spectrometry Study, ACS Catalysis, 2020, 10(21), pp. 12828–12840*
9. *Xu, S., Chen, H., Hardacre, C., Fan, X., Non-thermal plasma catalysis for CO_2conversion and catalyst design for the process, Journal of Physics D: Applied Physics, 2021, 54(23), 233001*
10. *Li, J., Chansai, S., Hardacre, C., Fan, X., Non thermal plasma assisted water-gas shift reactions under mild conditions: state of the art and a future perspective, Catalysis Today, 2022*

1.5. Required initial knowledge and skills of the PhD candidate

- knowledge on chemistry
- basic understanding of catalysis
- understanding of chemical and material's characterization techniques
- analytical thinking and skills
- open to challenging tasks and creative
- hard-working person, eager to learn

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

- ability to plan and organize laboratory work
- skilled in novel scientific techniques
- ability to solve research problems
- innovative thinking
- ready to work in an international research group