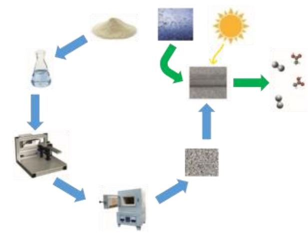
Title: Development of highly efficient sustainable renewable solar energy sources via InkJet technology

For further information or help with the writing of the proposal to be submitted, please contact:
Patrícia Guerreiro (piguerreiro@ciencias.ulisboa.pt), Manuel Minas da Piedade (memp@fc.ul.pt), or Liubov Belova (lyuba@kth.se)

Aim: Development of solar → hydrogen, solar → electricity, and hybrid conversion devices based on InkJet technology.

State of the Art

The demand for sustainable fossil-free energy sources has dramatically increased over the past decade, fostered by the recognition that a transition from fossil fuel to clean energy dependency needs to be quickly achieved to ensure a sustainable future for the planet.[1,2] Among the envisioned sustainable energy sources, solar energy has the largest potential to satisfy the future global needs due to its availability, accessibility in large quantities, true fossil-free nature, and reasonably efficient extraction/conversion means.



Perovskite based solar cells are one of the most promising solutions for the development of next generation solar devices because of their very good conversion efficiency, that can surpass 20%. Their fabrication is solution-based, involves substantially lower temperatures, and typically does not require vacuum equipment. However, there are substantial challenges with the currently available top-performing materials, the main being: (*i*) chemical composition based on toxic components (Pb and I) and (*ii*) very poor long-term stability.[3,4]
Currently available fossil-free energy sources (e.g. solar cells and wind generators) provide energy that is impossible to plan, and peaks of production are often mismatched with peaks of consumption. Thus, for these technologies to be successful, there is a need for efficient energy conversion and storage methods. Considering the exploding number of electric vehicles, Li-ion batteries do not constitute a sustainable energy storage solution for large scale needs, and hydrogen storage is a good alternative candidate. Direct solar-to-hydrogen conversion devices are especially interesting as theoretically they don't encounter substantial losses associated with intermediate conversion.[5]
This project aims at addressing both of these types of devices based on InkJet technology. InkJet-based fabrication is: (*i*) easy to scale up, (*ii*) waste-free, (*iii*) inexpensive, (*iv*) environmentally friendly, (*v*) energy efficient, (*vi*) sustainable, (*vii*) doesn't require use of toxic or scarce materials, (*viii*) compatible with flexible/bendable substrates, and (*ix*) allows direct digital patterning to a desired size and shape, which enables unique integration solutions.

Objectives

The work program will focus on:

(1) All-printed solar cells fabrication under ambient conditions.

(2) InkJet patterned high-efficiency solar-to hydrogen photocatalytic conversion devices that do not contain Pt or other rare/precious materials.

(3) Investigation of the interaction of raw, photovoltaic and photocatalytic materials with water and water vapor (humidity), through the calorimetric determination of wetting enthalpies and enthalpies of water vapor adsorption.

Objectives (1) and (2) will be mainly pursued at KTH (Sweden) and objective (3) mainly at FCUL (Lisbon).

General Methodology

All-printed perovskite solar cells will be prepared via InkJet technology. There are considerable on-going efforts world-wide for the development of scaled fabrication of perovskite solar cells, including InkJet-based methods. One aspect that makes this project unique is the development of a process that can fully work under ambient conditions, without any step requiring a clean room or glovebox. Furthermore, low fabrication temperature will have an enormous impact in reducing the energy investment (e.g. in comparison with Si technology requiring 1500°C for Si doping). Special attention will also be given to long-term stability of the cells and development of smart protective InkJet patterned coatings. This will bring our program **beyond the state-of-the-art** in perovskite photovoltaics.[6]

For solar-to hydrogen photocatalytic conversion we will explore catalysts consisting of abundant and readily available materials, mostly under the form of pure or mixed oxides, with and without metallic inclusions, in layered or patterned structures allowing the fine control of defects that affect the overall performance.[7] This will be a step **beyond the state-of-the-art** in photocatalytic H_2 production.

The development of the manufacturing methods involves designing the ink, as the composition of the ink (concentration of the active material, use of solvents and surfactants) has a profound effect on layer formation (via surface tension and viscosity), as well as on the drying dynamics and thickness of the single-pass layer and thus on microstructure of the final film. Furthermore, printing parameters like e.g. shape of the waveform, volume of the printhead, type of substrate and temperature also have a significant impact on the layer formation and drying/crystallization steps. As for solar cells the process will be optimized for low-temperature operation, in line with the sustainability goal. Curing and annealing temperatures will be optimized with the aid of thermoanalytical measurements as typically done in the optimization of this type of manufacturing methods.

A key issue to obtain efficient photovoltaic and photocatalytic devices is a fundamental understanding of their interaction with water. This aspect is important in photovoltaics for stability reasons and in photocatalysis because it determines the efficiency of the process to a large extent. The interaction of water with materials/devices of interest will therefore be investigated, starting with samples whose preparation has already been achieved. This will involve calorimetric experiments directed to the determination of wetting enthalpies by solution microcalorimetry and enthalpies of water vapor adsorption using Calvet microcalorimetry.[8] Tests of photovoltaic stability by exposing the samples to humidity in a Calvet calorimeter under irradiation will also be performed.

All these studies will be complemented by a variety of structural, optical, thermal, and functional properties characterizations, to be done at both sites or using already established collaborations, namely:

- Thermal analysis: Prof. Hermínio Diogo, Instituto Superior Técnico, ULisboa.
- Optical properties: Prof. Luís Santos, Instituto Superior Técnico, ULisboa.
- Test of performance in terms of photocatalytic activity for H_2 production: Prof. Cazorla-Amoros, University of Alicante.
- Photovoltaic accelerated and real-life field tests: Prof. Eugene A. Katz, Ben-Gurion University of the Negev, Israel.
- Quantum chemistry modeling: Prof. Cláudio Lousada, KTH, Sweden.

The results from the calorimetric studies on water interaction will be used as benchmarks for the validation of the quantum mechanical methodologies used by Prof. Cláudio Lousada to provide: (*i*) important guidelines for the synthesis and optimization of materials relevant for the work program; (*ii*) molecular insights into the mechanisms underlying materials function.

Supervision and PhD environment

This project will be supervised by Prof. Manuel Minas da Piedade (FCUL, ULisboa, Portugal) and Prof. Liubov Belova (KTH, Sweden).

Prof. Minas da Piedade is the head of the Molecular Energetics Group from Centro de Química Estrutural (FCUL site) and president of the Physical Chemistry Division of the Portuguese Chemical Society. He has considerable experience in the application of calorimetric methods to a variety of problems and systems, ranging from isolated molecules to solid forms or living cells. The facilities include all calorimetric and thermal analysis equipment needed for the project, as well as a diversity of characterization techniques, such as diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, powder (PXRD) and single-crystal (SCXRD) X-ray diffraction, or AFM. Centro de Química Estrutural is a research unit that has always been ranked excellent by the Portuguese national science foundation (FCT).

Prof. Belova is professor of Experimental Nanoscience, and PhD Program director at the KTH Department of Materials Science and Engineering. Prof. Belova has over 20 years of experience with inkjet patterning (as well as other types of additive 3D fabrication) of different functional materials for a wide range of applications. Her group has an in-house designed InkJet printing station, as well as facilities for annealing and curing the printed films. Through the KTH core facilities, the group has full access to state-of-the-art microstructural characterization, e.g. thermal analyzes, XRD, advanced microscopy (e.g. SEM/FIB, SPM tools), viscosimetry, and tensiometry.

The ongoing collaborations mentioned above will provide access to complementary facilities and expertise whenever needed. Thus, besides ULisboa and KTH the PhD student will be exposed to different international collaborations and research environments. This will result in versatile multi-disciplinary training that will have a positive impact on future career perspectives.

References

1. Gielen, D.; Boshell, F.; Saygin, D.; Bazilian, M. D.; Wagner, N.; Gorini, R. The Role of Renewable Energy in the Global Energy Transformation. *Energy Strateg. Rev.* **2019**, *24*, 38-50.
2. Holechek, J. L.; Geli, H. M. E.; Sawalhah, M. N.; Valdez, R. A Global Assessment: Can Renewable Energy Replace Fossil Fuels by 2050? *Sustainability* **2022**, *14*, 4792.
3. Lye, Y. E.; Chan, K. Y.; Ng, Z. N. A Review on the Progress, Challenges, and Performances of Tin-Based Perovskite Solar Cells. *Nanomaterials* **2023**, *13*, 585.
4. Lekesi, L. P.; Koao, L. F.; Motloung, S. V.; Motaung, T. E.; Malevu, T. Developments on Perovskite Solar Cells (PSCs): A Critical Review. *Appl. Sci.* **2022**, *12*, 672.
5. Song, H.; Luo, S. Q.; Huang, H. M.; Deng, B. W.; Ye, J. H. Solar-Driven Hydrogen Production: Recent Advances, Challenges, and Future Perspectives. *ACS Energy Lett.* **2022**, *7*, 1043-1065.
6. Lu, D. L.; Zhang, W.; Kloo, L.; Belova, L. Inkjet-Printed Electron Transport Layers for Perovskite Solar Cells. *Materials* **2021**, *14*, 7525.
7. Singh, V.; Lousada, C. M.; Jonsson, M.; Belova, L. M. Scalable InkJet-Based Additive Fabrication of Photocatalytic TiO_2 Thin Films. *ChemPhotoChem* **2022**, *6*, e202100212.
8. Martinho Simões, J. A.; Minas da Piedade, M. E. *Molecular Energetics: Condensed Phase Thermochemical Techniques*; Oxford University Press: New York, 2008; 182-183.