

UNIVERSITÀ DEGLI STUDI DI GENOVA
AREA RICERCA, TRASFERIMENTO TECNOLOGICO E TERZA MISSIONE

SERVIZIO RICERCA
SETTORE RICERCA NAZIONALE

IL RETTORE

Vista la Legge 9 maggio 1989, n. 168 - Istituzione del Ministero dell'Università e della ricerca scientifica e tecnologica e ss.mm.ii;

Visto lo Statuto dell'Università degli Studi di Genova;

Visto il Regolamento Generale di Ateneo;

Visto il Regolamento di Ateneo per l'Amministrazione, la Finanza e la Contabilità;

VISTA la legge 7 agosto 1990, n. 241 recante "Nuove norme in materia di procedimento amministrativo e di diritto di accesso ai documenti amministrativi" pubblicata sulla Gazzetta Ufficiale n. 192 del 18/08/1990 e s.m.i.;

VISTO il Decreto del Presidente della Repubblica 28 dicembre 2000, n. 445 (Disposizioni legislative in materia di documentazione amministrativa) e s.m.i.;

VISTO il Decreto Direttoriale MUR n. 341 del 15/03/2022 di emanazione di un Avviso pubblico per la presentazione di Proposte di intervento per la creazione di "Partenariati estesi alle università, ai centri di ricerca, alle aziende per il finanziamento di progetti di ricerca di base" nell'ambito del Piano Nazionale di Ripresa e Resilienza, Missione 4 "Istruzione e ricerca" – Componente 2 "Dalla ricerca all'impresa" – Investimento 1.3, finanziato dall'Unione europea – NextGenerationEU";

VISTO il Decreto Direttoriale MUR n. 1561 dell'11 ottobre 2022 Codice identificativo PE00000021, Acronimo NEST, Titolo "Extended Partnership Network 4 Energy Sustainable Transition" (CUP D33C22001330002) registrato alla Corte dei Conti il 04/11/2022 con prot. n. 2784 e relativi allegati;

CONSIDERATO che l'Università degli Studi di Genova è leader dello Spoke 4, dal titolo "Clean Hydrogen and Final Uses";

CONSIDERATO che gli Spoke possono emanare - nell'ambito dei limiti e con le modalità previste dall'Avviso - "bandi a cascata" finalizzati alla concessione di finanziamenti a soggetti esterni per attività coerenti con il progetto approvato;

VISTA la delibera della seduta del 27 settembre 2023 con cui il Consiglio di Amministrazione dell'Università degli Studi di Genova ha approvato il modello del "Bando a Cascata" per Organismi di Ricerca;

VISTO il Decreto del Direttore Generale n. 5418 del 14 novembre 2023 di nomina del Responsabile del Procedimento;

VISTO il Decreto del Rettore n. 366 del 24 gennaio 2024 di emanazione del Bando a cascata per il



finanziamento di proposte di intervento per attività di ricerca svolte da Organismi di Ricerca nell'ambito del Programma di ricerca "Extended Partnership Network 4 Energy Sustainable Transition – NEST" PE00000021 - SPOKE N. 4 - CUP D33C22001330002 di cui al Decreto direttoriale n. 1561 del 11 ottobre 2022, registrato dalla Corte dei Conti il 04/11/2022 n. 2784;

CONSIDERATO che alla data di scadenza per la presentazione delle proposte progettuali, fissata entro e non oltre il giorno 29 febbraio 2024, per la **Tematica I - Innovation for green hydrogen production from biomass** era pervenuta a mezzo PEC all'indirizzo air3@pec.unige.it la seguente proposta:

PROPONENTE: Università degli Studi di Pavia - Prot. 14180_26.02.2024

TITOLO PROPOSTA: PER2H – Development of High Entropy Perovskite Oxide-Based Photocatalysts for Green Hydrogen Production from Biomass

TENUTO CONTO che con D.D. 1264 del 18 marzo 2024 la Responsabile del procedimento, Ing. Patrizia Cepollina, ha ritenuto ricevibile, ammissibile e conforme la proposta sopra citata;

CONSIDERATO che nel Bando è previsto che la valutazione di merito tecnico-scientifico dei progetti pervenuti sia affidata ad una Commissione composta da almeno tre esperti esterni al Partenariato, indipendenti e competenti dell'Area tematica dello Spoke;

VISTO il D.R. 1025 del 28 febbraio 2024 di emanazione dell'Avviso di manifestazione di interesse per la costituzione di un Albo di esperti indipendenti a supporto della valutazione di merito dei progetti PNRR presentati sui bandi a cascata del progetto NEST – "Extended Partnership Network 4 Energy Sustainable Transition";

VISTO il D.R. n. 1477 del 26 marzo 2024 che ha costituito l'Albo a supporto della valutazione dei progetti presentati in risposta al bando a cascata, emanato dall'Università degli Studi di Genova in qualità di Leader dello Spoke 4 del progetto NEST – CUP D33C22001330002, con D.R. n. 366 del 24/01/2024;

VISTO il D.R. n. 1549 del 28 marzo 2024 con cui è stata nominata la Commissione di valutazione delle proposte pervenute in risposta al bando a cascata indicato nelle premesse del presente decreto;

ACQUISITO il verbale della Commissione di Valutazione della seduta del 17 maggio 2024 (Prot. 44296 del 21.05.2024) per la Tematica I - Innovation for green hydrogen production from biomass;

VISTO il verbale della riunione del 21 maggio 2024 (Prot. 45085 del 22 maggio 2024) di presa d'atto dei Verbali della Commissione di valutazione;

TENUTO CONTO che in data 27 maggio 2024 è stata inviata all'Università degli Studi di Pavia la comunicazione Prot. 46794 in cui si rendevano noti gli esiti della procedura e si richiedeva la documentazione propedeutica all'adozione del provvedimento di ammissione del finanziamento;

TENUTO CONTO che la documentazione, ricevuta con nota Prot. n. 48101 del 29 maggio 2024 è stata ritenuta conforme a quanto previsto nel bando a cascata di cui al Decreto del Rettore n. 366 del 24 gennaio 2024, indicato nelle premesse del presente decreto,



DECRETA

ART. 1

L'ammissione a finanziamento del progetto "PER2H – Development of High Entropy Perovskite Oxide-Based Photocatalysts for Green Hydrogen Production from Biomass" per la **Tematica I - Innovation for green hydrogen production from biomass** con soggetto proponente Università degli Studi di Torino - come rappresentato negli Allegati B e C alla proposta presentata con domanda di partecipazione Prot. 14180 del 26 febbraio 2024

ART. 2

L'entità dell'agevolazione concessa, a fondo perduto, ammonta a 120.000 euro complessivi come rappresentati nell'allegato C alla proposta presentata con domanda di partecipazione Prot. 14180 del 26 febbraio 2024. L'agevolazione è pari al 100% dei costi di progetto trattandosi di attività di ricerca fondamentale per Organismi di Ricerca. L'agevolazione è concessa a valere sui fondi PNRR - Programma "NEST – Extended Partnership Network 4 Energy Sustainable Transition" Codice PE00000021 finanziato dalla Missione 4, Componente 2, Investimento 1.3, ai sensi del Decreto Direttoriale N. 1561 del 11 ottobre 2022, registrato dalla Corte dei Conti il 04/11/2022 n. 2784 iscritto al Bilancio di Ateneo sul progetto UGOV 100025-2022-LM-PNRR-PE_NEST_B_C_RICERCA_DIP- (CUP D33C22001330002);

ART. 3

Le attività di realizzazione del progetto, come indicate dettagliatamente negli Allegati B e C alla domanda di finanziamento, non potranno essere superiori a 12 mesi a decorrere dalla data di sottoscrizione del Contratto, salvo quanto previsto all'art. 6.3 del bando.

Le attività dovranno comunque essere concluse entro e non oltre il 31 agosto 2025, salvo proroghe del Programma di ricerca NEST concesse dal MUR, affinché siano rendicontate in tempo utile per consentire la chiusura del Programma di ricerca NEST il cui termine è attualmente previsto al 31 ottobre 2025.

ART. 4

Il presente atto sarà pubblicato sul sito UniGe <https://unige.it/progetti-finanziati-dal-pnrr> e sul sito <https://fondazionenest.it> - sezione Bandi.

Il documento informatico originale sottoscritto con firma digitale sarà conservato presso l'Area Ricerca, Trasferimento Tecnologico e Terza Missione.

IL RETTORE

Prof. Federico DELFINO

(documento firmato digitalmente)



ALLEGATO B

PE00000021

**“PNRR MUR - M4C2 – NEST - Extended Partnership
Network 4 Energy Sustainable Transition”**

SPOKE N. 4

CUP D33C22001330002

Research proposal

Innovation for green hydrogen production from biomass

**PER2H – Development of High Entropy Perovskite Oxide-
Based Photocatalysts for Green Hydrogen Production from
Biomass**

- Università degli Studi di Pavia
- Lorenzo Malavasi, Andrea Speltini
- Proposal duration in months: 12

<i>ROLE IN THE PROJECT</i>	<i>NAME</i>	<i>SURNAME</i>	<i>INSTITUTION/ DEPARTMENT</i>	<i>QUALIFICATION</i>	<i>YOUNG (under 40 al 31.12.2023)</i>	<i>F/M</i>
Principal Investigator (PI)	Lorenzo	Malavasi	University of Pavia/Chemistry	Full Professor		M
Co-Principal Investigator (co-PI)	Andrea	Speltini	University of Pavia/Chemistry	Associate Professor	Yes	M
Investigator	Costanza	Tedesco	University of Pavia/Chemistry	PhD Student	Yes	F
Investigator	Luca	Betti	University of Pavia/Chemistry	PhD Student	Yes	M
Investigator	Francesca	Merlo	University of Pavia/Chemistry	PostDoc	Yes	F

ABSTRACT

PER2H project is addressed to develop new photoactive materials with improved efficiency for the solar light-driven photocatalytic production of hydrogen gas from biomass in aqueous solution, to meet the increasing demand for massive clean H₂ production. This will be achieved by new heterojunctions, simply and quickly prepared by spray-pyrolysis coupling P25 titanium dioxide and g-C₃N₄ with high-entropy perovskite oxides (HEPOs), namely La(B)O₃ (B=Ni, Fe, Mn, Co, Zn). The composites will benefit from the high oxidation capability of titania combined with the enlarged visible light absorption and longer lifetime of the charge carriers involved by the coupling with the HEPOs. Similarly, HEPOs composites with graphitic carbon nitride, which will be synthesized in laboratory by a consolidated route from low-cost precursors (i.e., dicyandiamide), will be prepared. All materials will undergo full characterization by several techniques XRD, HR-SEM, XRF, TGA, BET, Uv-VIS and PL spectroscopies. After a preliminary screening of the catalytic activity of the hybrid semiconductors under simulated solar light, evaluated based on the H₂ evolution from glucose aqueous solution, the work will be devoted to develop new photocatalytic systems directly in food industry wastewater, i.e., from beer and rice production. An investigation on the operational factors involved in the photocatalytic process will be studied to maximize H₂ production under sustainable conditions, that is using waste biomass, under natural sunlight. A prototype lab-scale photoreactor will be set up for continuous H₂ production using the best performing heterojunction, which will be directly immobilized by spray-pyrolysis onto glass supports for a facile catalyst recovery and recycling, further improving the sustainability of the process.

RESEARCH PROPOSAL

Section a. State-of-the-art and objectives

Nowadays, the increasing global crisis of energy shortage and environmental issues are becoming serious threats to the long-term development of human society. Governments and scientists are trying to find out green technologies to address such concerns. Among the potential solutions, semiconductor-based photocatalysis has emerged predominantly as it is considered a costless, renewable, clean, and safe technology, which requires only the inexhaustible solar light as a driving force, and a suitable semiconductor as a photocatalyst to conduct catalytic reactions for a variety of applications, including H₂ production from water.¹ H₂ is an appealing storable energy source because its conversion in fuel cells efficiently generates energy, releasing water as the only by-product. To date, most of the produced H₂ derives from natural gas through steam-methane reforming, and only ~ 5% is obtained from renewable resources, mostly via water electrolysis. However, producing H₂ from natural gas poses some concerns like the restricted availability of fossil fuels and large amount of released CO₂. In light of this scenario, the development of innovative procedures both to produce H₂ from renewable materials, such as biomass and water, and to store the same fuel in a safe and efficient way in cheap and convenient materials, is strongly required and constitutes hot research topics. With reference to the photocatalytic route for hydrogen gas retrieving, presently the keywords are greenness, safety, renewability, efficiency, circular economy and sustainability. Of course, combining all these aspects really represents the big challenge the scientific community still faces, but, at the same time, it is highly exciting and inspiring for researchers. Many semiconductors have been identified as potential photocatalysts under UV or visible light, such as ZnO, CdS, TiO₂, SnO₂, BiVO₄, Cu₂O, Fe₂O₃ etc., and more recently also organic materials as graphitic carbon nitride, and perovskites.²⁻⁶ Among these, TiO₂ is still used as the benchmark due to its chemical stability, low cost and non-toxicity. However, a serious drawback of all those photocatalysts is the low efficiency caused by the fast recombination of the charge carriers. Improving charge carriers separation is thus the **first key point**, and a way is to develop semiconductor composites that assure the opposite migration of electrons and holes by conduction-band (CB) and valence-band (VB) offsets. Strategies to improve charge carrier dynamics most employed to date are: rational design of heterojunctions; deposition of co-catalysts (e.g. noble metals) onto the catalytic surface (favouring also the surface reaction by reducing the activation energy); and control over particle size to shorten the diffusion pathway of the charge carriers.^{2-4,7,8} A **second key point** for a more rewarding and sustainable photocatalysis is to shift light absorption to the visible region. As a matter of fact, regardless of the advances achieved on titania-based photocatalysis for solar energy conversion, the practical application of TiO₂ is drastically limited because of the poor harvesting of natural sunlight. In fact, TiO₂ absorbs mainly the UV component of solar light (< 387 nm), that represents only 4-5% of the solar radiation spectrum. Finally, relating to H₂ evolution from water, several photocatalytic systems have been improved by addition of organic additives as the sacrificial agents that, undergoing oxidation, are able to enhance water reduction to give gas phase H₂. In this context, the **third key point** for a sustainable photocatalysis is the reuse of waste biomass. Beside fine chemicals such as triethanolamine, glycerol, alcohols etc., also insoluble polysaccharides and industrial wastewaters rich in organic sacrificial matter were proved (also by present PI and co-PI) to be applicable for this purpose.⁹⁻¹⁴ Considering the actual state-of-the-art, it is clear that **a fundamental caveat for a concrete development of all these technologies is still related to materials characteristics enabling photoreactions**. In the past 12 years, the proponents focused their research on sustainable systems and innovative photocatalysts for H₂ production. Among other results, we provided a series of novel stable perovskites with high visible-light absorption which have been used for hydrogen photogeneration both from water and biomasses and whose properties have been enhanced through the creation of suitable heterojunctions with g-C₃N₄.^{5,6,12,13} Carbon nitride was also important object of the members of the present project in terms of modulation of its properties through chemical modification and rationalization of photocatalytic properties.¹⁵⁻¹⁷

Aim of PER2H project is to develop new photoactive materials with improved efficiency for the solar light-driven photocatalytic production of hydrogen gas from biomass substrates, to meet the demand for massive clean H₂ production. Photocatalysis is indeed a viable alternative to the high energy-

consuming approaches as the thermochemical, electrochemical and biochemical ones, thus it deserves much more investigation. In this respect, the project will exploit the use of innovative High Entropy Perovskite Oxides (HEPO) photocatalysts as highly efficient and light-absorbing materials for hydrogen photogeneration. Nanometric HEPOs, characterized by structural heterogeneity and cation diversity, show promise in a wide range of applications. They demonstrate catalytic capabilities in complex chemical reactions, serve as energy storage devices for lithium-ion battery systems, and contribute to advances in fuel cell technologies. The focus on oxygen vacancies is crucial in this context, as these defects, which result from a lack of oxygen atoms, significantly influence the electronic and catalytic properties of the materials. Harnessing and controlling these defects can improve system performance, particularly in photocatalysis. The high entropy of nanometric perovskite oxides is particularly advantageous, giving the material considerable flexibility in both physical and chemical properties. The formation of a heterojunction with HEPOs is a particularly fascinating and under-explored area of research. The nanomorphology allows close contact and homogeneous integration of the perovskite into the heterojunction. In addition, the oxygen vacancies resulting from the chemical structure would act as active sites for photocatalysis. Creating a heterojunction with another semiconductor as proposed in this project (namely with TiO_2 and $\text{g-C}_3\text{N}_4$), and using these materials, constitute an innovative perspective to enhance the efficiency and stability of the photocatalysis process, overcoming current limitations. Specifically, we will focus on the structural and photocatalytic study of HEPOs with general formula $\text{La}_{1-x}\text{A}_x(\text{B})\text{O}_3$ ($\text{B}=\text{Ni, Fe, Mn, Co, Zn}$) and alkaline-earth dopants on the A-site (Ca, Mg and Sr). We aim to correlate the presence of oxygen vacancies with the type and quantity of dopant, investigating both the band alignment and the electronic schema type in the heterojunction. Additionally, the project aims to examine the effect and quantity of vacancies on hydrogen production from biomass solutions. In conclusion, exploring this heterojunction, through the utilization of nanometric HEPOs, represents an advanced, promising, and innovative approach to boost the photocatalytic hydrogen production.

Based on the above considerations, the main objects of the project are:

- Provide innovative photoactive materials based on HEPOs of general formulas $\text{La}(\text{B})\text{O}_3$ ($\text{B}=\text{Ni, Fe, Mn, Co, Zn}$) for H_2 production from aqueous biomass substrates covering a wide light absorption spectrum (from UV to NIR), showing long-lived photogenerated charges (>500 ns), high quantum efficiencies (50%), ease of fabrication, low-cost, and based on earth-abundant elements;
- Fabrication of HEPO-based composites to further improve the catalytic properties and to power the overall reactions involving both oxidation and reduction under visible light illumination. Such composites will see the combination of tailored HEPOs with TiO_2 and $\text{g-C}_3\text{N}_4$;
- Manufacture a lab-scale photoreactor with the best performing photocatalysts developed in the project. To validate the proposed technology, a continuous reactor for hydrogen photogeneration will be manufactured (see details in section b)).

The principles of green chemistry and sustainability will guide the experimental work and final objectives of the plan. Indeed, the catalytic composites will be first tested in model biomass derivatives solution, then directly in wastewaters from the agri-food sectors under natural sunlight, with the intention to combine biomass recovery/valorisation with H_2 evolution. Last but not least, a significant advancement of the present project will be the use of supported HEPOs composites, providing an appealing strategy to overcome the main drawbacks of slurry reactors, such as nanoparticle separation from water and toxicity concerns due to their release in the environment. To conclude, **PER2H project spans a TRL from 1 to 4, and has a significant focus in developing novel devices/technologies for effective H_2 photogeneration from biomasses through the development of innovative and efficient catalytic systems.** We believe that the results achieved in the project will have the potential for future exploitation of the results towards the market, in a medium-to-long term vision, providing efficient devices and industry substitutes to fossil fuels. In addition, the solution proposed in the project art stands alone and can provide solar fuels in a decentralized way.

Section b. Methodology

PER2H project is composed of distinct sequential stages, namely the analysis of the technical-scientific aspects involved in the process under study in the framework of the actual knowledges, the development of the proposed innovation, and the experimental testing, evaluation and validation of the proposed solutions, which will be accomplished through the following Work-Packages (WPs). These are reported hereafter together with the expected duration in months (M).

WP1: Analysis of the state-of-the-art and of the actual technologies/approaches to identify the innovation level of the proposed solution (M01-03)

In this WP we will perform an accurate review of the current state-of-the-art. In particular, we will focus on the analysis of the reference process and of the technological challenge to be addressed and of its complexity. In addition, the actually existing technologies/approaches will be fully reviewed in order to identify the innovation level of the proposed solution.

WP2: Design of innovative photoactive catalysts based on HEPO heterojunctions (M02-06)

T2.1: Synthesis of mixed nanometric HEPOs. We plan to synthesize nanometric HEPOs by spray-pyrolysis method. This method involves spraying a nitrate solution of the precursor cations, in precise concentrations and stoichiometric proportions, after which the aerosol passes through a high-temperature chamber (1000°C) where oxidation takes place and the formation of the perovskite oxide occurs. Stoichiometries that will be considered are: $\text{La}_{1-x}\text{A}_x(\text{Mn}_{0.25}\text{Zn}_{0.25}\text{Co}_{0.25}\text{Fe}_{0.25})\text{O}_3$ and $\text{La}_{1-x}\text{A}_x(\text{Mn}_{0.25}\text{Ni}_{0.25}\text{Co}_{0.25}\text{Fe}_{0.25})\text{O}_3$ with $\text{A}=\text{Ca}$, Mg and Sr and $x=0, 0.20$, and 0.40 . Samples will be fully characterized by x-ray powder diffraction (XRD), high-resolution scanning electron microscopy (HR-SEM, with elemental analysis), X-ray fluorescence spectroscopy (XRF), surface area measurement (BET method) and thermo-gravimetric analysis (TGA). Optical properties will be investigated by UV-VIS and photoluminescence (PL) spectroscopies.

T2.2: Synthesis of heterojunction based on nanometric HEPOs. In this task, we will couple the prepared nanometric HEPOs with TiO_2 (Evonik AEROXIDE® P25) and nanosheets of $\text{g-C}_3\text{N}_4$. These last will be prepared from dicyandiamide according to methods already optimized by the UNIPV group.⁷ Heterojunctions will be obtained by suspending appropriate stoichiometric amounts of HEPO and the second semiconductor in water-methanol mixtures, the suspensions will be sonicated for 5 min, then mixed and placed on heating plate (60°C) under vigorous stirring until dry powder is obtained. Then, we will prepare heterojunction with different ratios between the HEPO and the second semiconductor (TiO_2 and $\text{g-C}_3\text{N}_4$). A full characterization of the prepared heterojunctions will be performed as for the samples of T1.1.

WP3: Photoactivity of engineered materials (M06-09)

T3.1: Preliminary photocatalytic tests. In the first part of this WP, the prepared heterojunctions will be tested for H_2 production from water and their photocatalytic activity will be compared to that of the commercial Evonik AEROXIDE® P25 TiO_2 (77.1% anatase, 15.9% rutile, 7% amorphous TiO_2 , particle size 10-50 nm, surface area 60.8 m^2/g), the benchmark catalyst in the control trials, to assess the role of the high-entropy oxides deposited on the titania particles.¹⁸ A series of lab-scale photoproduction tests will be performed in triplicate to evaluate the H_2 evolution rates (HERs) under standard test conditions, that is working in aqueous solutions of probes sacrificial agents (0.1 M glucose), using platinum as the conventional, reference co-catalyst (0.5 wt%). Samples will be irradiated (4 h, 500 W/m^2 , magnetic stirring) in Pyrex glass containers (30 mL capacity) equipped with sleeve stopper septa. After addition of the catalyst (1 g/L) and deoxygenation by N_2 bubbling (20 min), irradiation will be done by a Solar Box, equipped with a UV outdoor filter of soda lime glass IR treated, will be used as the solar light simulator. The evolved gas will be determined by gas chromatography (GC) through injection of proper volumes of the vessel headspace in a GC system equipped with a thermal conductivity detector (TCD).

T3.2: Hydrogen production from biomasses. On the basis of the HERs obtained in T3.1, the best catalyst will be selected for H_2 photogeneration from (waste)biomass, in particular sugar-rich wastewaters from the agri-

food sector will be tested, as brewery and rice industry wastewaters. The photoreaction will be optimized by a chemometric approach (factorial experimental design) taking into account in a multivariate way the main variables affecting the photocatalytic system, *viz.* biomass amount (waste dilution), catalyst concentration (0.1-2 g/L) and co-catalyst amount (0-3 wt%). Experimental conditions for irradiation will be analogous to T3.1.

WP4: Lab-scale prototype photoreactor for continuous H₂ production (M02-12)

T4.1: Deposition of photocatalyst. As a noteworthy technical advancement, to streamline the experimental workflow, in this task the best performing heterojunction resulting from WP3 will be deposited onto glass substrates, fully eliminating the time-consuming and expensive procedures for the catalyst recovery after irradiation. Deposition will be realized by means of spray deposition starting from an aerosol of the precursor mixture made of powdered semiconductor (TiO₂ or g-C₃N₄) and metals nitrates. Annealing of the substrate will provide the requested continuous film, with no need for binders. The film of the heterojunction will be fully characterized as in WP1. However, the surface morphology will be further investigated by atomic force microscopy (AFM).

T4.2: Photocatalytic test in the prototype photoreactor. The films prepared and optimized in T4.1 will be placed into an *ad hoc* manufactured photoreactor, schematically shown in Fig. 1, where a continuous flow of water containing biomass will pass in contact with the photocatalytic bed, and the produced hydrogen will be collected as well in continuous mode through a dedicated injection switch valve in the GC instrument. Design of the photoreactor has been already devised and its manufacture will be started soon after the start of the project. We already secured two potential providers which will deliver the photoreactor in 30-45 days after order. We will look for the most rewarding experimental conditions (geometry, exposed surface area of the supported catalyst, amount of photoactive composite per substrate) by in-laboratory irradiation and after that, the performance of the system will be explored under natural solar light (outdoor conditions), and catalyst reusability tests will be performed as well, aiming at a further improvement of the sustainability of the process.

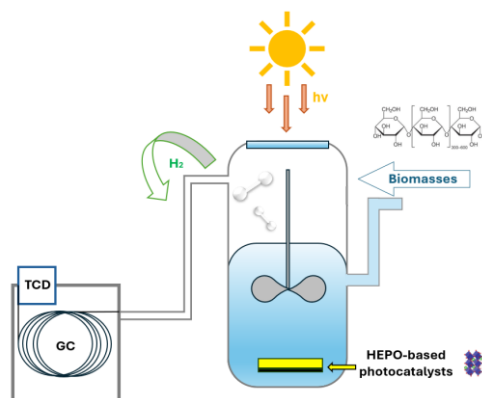


Fig. 1 – Schematic representation of the prototype photoreactor

WP5: Communication and Dissemination (M01-12)

Even though the project has a limited duration of 12 months, we expect to provide an active communication and dissemination of the project results through audience-centred activities, including seminars for academics and participation in national/international conferences. In particular, we expect to publish at least 3 papers based on the projects results. Publications resulting from this project will be published in open access journals. In accordance to the FAIR policy, scientific articles will be deposited in online institutional repositories, immediately after their publication. Sensitive data will be considered for IPR protection and, where and if pertinent, part of the results could also be object of patenting. As requested by the call, technical reporting will be delivered at the end of WP 1 (M03) and at the end of the project (M12).

References

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- (2) Dong, X.; Cheng, F. Recent Development in Exfoliated Two-Dimensional g-C₃N₄ Nanosheets for Photocatalytic Applications. *J. Mater. Chem. A* **2015**, *3* (47), 23642–23652. <https://doi.org/10.1039/C5TA07374J>.
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Section c. Available instrumentations and resources

Analytical tools: HPLC-MS/MS, HPLC-UV, HPLC-FD, GC-TCD, GC-FID, GC-MS, ICP-OES, ICP-MS, UV-vis spectrophotometers, COD/TOC analyzer, solar box, XRD diffractometers (Cu and Mo radiation), High resolution SEM, TGA, DSC, AFM, XRF, profilometer, Uv-VIS and PL spectrometers.

Section d. GANTT diagram

WP	Task	Months											
		1	2	3	4	5	6	7	8	9	10	11	12
1		Yellow	Yellow	Yellow									
2	T2.1		Blue	Blue	Blue								
	T2.2				Blue	Blue	Blue						
3	T3.1						Yellow	Yellow					
	T3.2							Yellow	Yellow	Yellow			
4	T4.1		Green	Green	Green	Green							
	T4.2						Green	Green	Green	Green	Green	Green	Green
5		Blue	Blue	Blue	Blue	Blue	Blue	Blue	Blue	Blue	Blue	Blue	Blue

Section e. Milestones, Deliverables and KPI

List of Deliverables

Number	Deliverable name	Short description	WP number	Delivery date (in months)
1	Literature review	Document describing state-of-the-art to identify innovation of proposed solutions	1	03
2	HEPOs	Synthesis of innovative HEPOs	2	05
3	Heterojunctions	Optimization of HEPO-based heterojunctions	2	07
4	H ₂ photoproduction	Optimization of H ₂ photogeneration from biomass by application of the heterojunctions	3	09
5	Catalyst	Optimization of the photocatalyst deposition on solid substrate	4	08
5	Photoreactor	Manufacture of the photoreactor	4	04
6	Experimental set-up	Optimization of the best experimental conditions for efficient photocatalysis inside the photoreactor	4	08

List of Milestone

Milestone N°	Milestone name	Related WP(s)	Due date (in months)	Means of verification
1	Report Step 1	1	03	Availability of report on Step 1
2	HEPO-based heterojunctions	2	07	Chemical/structural analysis, experimental results of basic characterization
3	Optimized photoactive heterojunctions	3	09	H ₂ photogeneration by biomasses against KPIs
4	Photoreactor	4	12	Optimized H ₂ photogeneration from biomasses in the photoreactor

List of KPIs

Objective	Results	KPI	Measure
Provide innovative photoactive materials based on HEPOs	Optimize synthetic strategy, chemical composition, particle morphology, heterojunction creation	Improving preparation routes and nanometric morphology vs state-of-the-art	Select the input materials to be investigated for photocatalytic hydrogen production
Performing a successful H ₂ production from biomasses	Optimize photocatalysts deposition, photoreactor configuration	Obtain hydrogen evolution rates (HER) from recovered biomasses above state-of-the-art values (>10 mmol/h/g)	Measurement of HER values and apparent quantum efficiency

Annexes: Curriculum vitae research team

Curriculum vitae PI

PERSONAL INFORMATION

Family name, First name: Malavasi, Lorenzo

Researcher unique identifier (ORCID): 0000-0003-4724-2376

Date of birth:

URL for web site: malavasi.unipv.it

• EDUCATION

- | | |
|------|--|
| 2003 | PhD
Department of Chemistry, University of Pavia, Italy
Supervisor: Prof. Giorgio Flor |
| 1999 | Master
Department of Chemistry, University of Pavia, Italy |

• CURRENT POSITION

- | | |
|--------|---|
| 2021 – | Full Professor
Department of Chemistry, University of Pavia, Italy |
|--------|---|

• PREVIOUS POSITIONS

- | | |
|-------------|--|
| 2015 – 2021 | Associate Professor
Department of Chemistry, University of Pavia, Italy |
| 2009 – 2015 | Assistant Professor
Department of Chemistry, University of Pavia, Italy |

• FELLOWSHIPS AND AWARDS

- | | |
|------|---|
| 2008 | Alfredo di Braccio" per la Chimica dell'Accademia Nazionale dei Lincei, Roma. |
| 2005 | Young Scientist Award" dell'"International Conference on Perovskites", EMPA, Dubendorf, Swiss |

• SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS (if applicable)

- | | |
|-------------|-----------------|
| 2008 – 2024 | 12 PhD Students |
| 2014 – 2024 | 8 PostDocs |

Department of Chemistry, University of Pavia, Italy

- **ORGANISATION OF SCIENTIFIC MEETINGS (if applicable)**

2024 MATSUS24. Symposium Organizer “Metal Halide Perovskite Photocatalysis”/Spain Please
2012 NONSTOICHIOMETRIC COMPOUNDS. Conference Chair/Italy

- **INSTITUTIONAL RESPONSIBILITIES (if applicable)**

2018 – Deputy Director of the Chemistry Department, University of Pavia/Italy
2017 – Member of the PhD School in Chemistry Board, University of Pavia/Italy
2018 – 2021 Member of Accademia Senate, University of Pavia/Italy
2017 – Member of the INSTM Board and Representative of the Pavia Research Unit, INSTM/Italy

- **REVIEWING ACTIVITIES (if applicable)**

2018 – Review panel member, National Science Foundation / Poland
2020 – 2021 Review panel member, Puglia Sviluppo / Italy
2016 – 2023 Review panel member, VQR / MUR/ Italy
2020 – Reviewer, ERC/European Commission
2010- Reviewer for several international journals, among other: JACS, Nature, Science, Nature Materials, Angewandte Chemie, JPCL, Science Advances, Nature Energy, Joule.

- **MAJOR COLLABORATIONS (if applicable)**

Filippo De Angelis, Computational Modelling, Department of Chemistry, University of Perugia /Italy
Annamaria Petrozza, Advanced Spectroscopy, Optoelectronic Group, IIT/Italy
Michele Saba, Pump Probe Spectroscopy, Department of Physics, University of Cagliari/Italy

Appendix: All current grants and on-going and submitted grant applications of the PI and Co PI (Funding ID)

Mandatory information (does not count towards page limits)

Current grants (Please indicate "No funding" when applicable):

<i>Project Title</i>	<i>Funding source</i>	<i>Amount (Euros)</i>	<i>Period</i>	<i>Role of the PI</i>	<i>Relation to current proposal</i>
A bio-inspired chemical approach for agro-industrial waste valorization (BEAGLE)	MUR/PNRR	225000	2023-2025	Principal Investigator	No direct relation

Re-Evolutionary solar fuel production envisioning water stable lead-free perovskites exploitation - REVOLUTION	MUR/PNRR	203624	2023-2025	Research Unit PI	Photocatalysis but with different materials and not on biomass
Tuning physical properties of chiral perovskite at high pressure (ProPerHP)	MAECI	81900	2023-2025	Principal Investigator	No relation
CHIRAL HYBRID ORGANIC-INORGANIC METAL HALIDES: A PLATFORM FOR EMERGING ELECTRONICS	Pathfinder Challenge	3900000	2023	Principal Investigator	<u>Submitted</u> , no relation

Curriculum vitae CO-PI

PERSONAL INFORMATION

Speltini, Andrea

Researcher unique identifier: ORCID 0000-0002-6924-7170

Date of birth:

URL for web site:

<https://unipv.unifind.cineca.it/resource/person/673708>

<https://chimica.dip.unipv.it/it/ricerca/linee-e-gruppi-di-ricerca/chimica-analitica/studi-la-produzione-fotocatalitica-di-h2-verde>

• EDUCATION

- 2011 PhD
 Department of Chemistry, University of Pavia, Italy
 Supervisor: Prof. Antonella Profumo
- 2008 Master
 Department of Chemistry, University of Pavia, Italy

• CURRENT POSITION(S)

- 2022 – Associate Professor
 Department of Chemistry, University of Pavia, Italy

• PREVIOUS POSITIONS

- 2018 – 2021 Assistant Professor (RTD A)
 Department of Drug Sciences, University of Pavia, Italy
- 2011 – 2018 Post-doc Research Fellow
 Department of Chemistry, University of Pavia, Italy

• FELLOWSHIPS AND AWARDS

- 2011 EUROANALYSIS XVI: Poster Prize awarded for excellent presentation of particularly significant innovative analytical research

• SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS

- 2010 – 31 Master Students (Thesis Correlator)
Department of Chemistry, University of Pavia, Italy
- 2021 – 5 Master Students (Thesis Relator)
Department of Chemistry and Department of Drug Sciences, University of Pavia, Italy
- 2022 – 1 Ph.D student (Thesis co-Supervisor)
Department of Chemistry, University of Pavia, Italy

• INSTITUTIONAL RESPONSIBILITIES

- 2021 – Member of the Tutoring Commission (“Commissione Tutorato”), Department of Drug Sciences, University of Pavia, Italy
- 2021 – Member of the Chemistry Commission of Almo Collegio Borromeo, Pavia, Italy

• REVIEWING ACTIVITIES

- 2010 – Reviewer for international peer-reviewed journals: Analytical and Bioanalytical Chemistry, Analytica Chimica Acta, Arabian Journal of Chemistry, Analytical Methods, Analytical Chemistry, Applied Catalysis B: Environmental, ACS Applied Materials & Interfaces, Applied and Environmental Soil Science, Bioanalysis, Chemical Engineering Journal, Chemosphere, Chemical Physics Letters, Chirality, Chromatographia, Desalination and water treatment, Ecotoxicology and Environmental Safety, Environmental Technology, Environmental Science and Technology, Environments, Food Chemistry, Fuel, International Journal of Environmental Analytical Chemistry, International Journal of Environmental Research and Public Health, International Journal of Hydrogen Energy, Industrial Engineering Chemistry Research, International Journal of Analytical Chemistry, Journal of Physics and Chemistry of Solids, Journal of Chromatographic Science, Journal of Chromatography A, Journal of Food Composition and Analysis, Journal of Chemistry, Journal of Pharmaceutical and Biomedical Analysis, Microchimica Acta, Nano, Photochemical & Photobiological Sciences, Journal of Separation Science, Sensors & Actuators: B. Chemical, Separation Science Plus, Science of the Total Environment, Talanta, Water Research
- 2020 – Editorial Board Member of International Journal of Environmental Research and Public Health, section “Environmental Science and Engineering”
- 2020 – Editorial Board Member of Catalysis, section “Photocatalysis”
- 2022 – Associate Editor of Frontiers in Environmental Chemistry
- 2023 – Evaluator of the project “Rational design and preparation of thermo-sensitive hydrogels for the capture and preconcentration of pesticides from aqueous matrices” project N° 1240126, 2024 Regular Fondecyt National Projects Competition (Chile)

• MEMBERSHIPS OF SCIENTIFIC SOCIETIES

- 2010 – Member of Italian Chemistry Society (SCI), Analytical Chemistry division, and

2022 – interdivisional group of Separation Science
Member of European Chemistry Society-Analytical Chemistry division (EuChemS-DAC),
Sample Preparation network/Green Sample Preparation working group

• MAJOR COLLABORATIONS

1. Prof. Massolini and Prof. Calleri, Department of Drug Sciences, University of Pavia (Italy): design, preparation and analytical application of (modified)high internal phase emulsions polymers for drugs extraction in various matrices
2. Prof. Ferretti, Department of Chemistry and Industrial Chemistry, University of Genoa (Italy): development and evaluation of sustainable photocatalysts for hydrogen production from water
3. Prof. Anticò, Department of Chemistry, University of Girona (Spain): preparation of biochar-modified polymer films for extraction of organic compounds/contaminants in complex matrices

Appendix: All current grants and on-going and submitted grant applications of the PI and Co PI (Funding ID)

Mandatory information (does not count towards page limits)

Current grants:

<i>Project Title</i>	<i>Funding source</i>	<i>Amount (Euros)</i>	<i>Period</i>	<i>Role of the co-PI</i>	<i>Relation to current proposal</i>
PRIN 2022 Prot. 2022HXZ3BK “Waste biomass valorisation for green H ₂ production by application of new TiO ₂ -Carbon Dots photocatalysts supported on magnetic zeolites obtained from industrial wastes”	UE/MUR	200000	2023-2025	Principal Investigator	Photocatalysis but with different catalysts and preparation routes
PRIN 2022 PNRR Prot. P2022HSWX “A bio-inspired	MUR/PNRR	225000	2023-2025	Permanent staff member of the Pavia University research unit	No direct relation



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DI RIPRESA E RESILIENZA



chemical approach for agro- industrial waste valorization (BEAGLE)”					
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Curriculum vitae (max. 3 pages)

PERSONAL INFORMATION

Family name, First name: Tedesco Costanza

Researcher unique identifier(s) (such as ORCID, Research ID, etc. ...): <https://orcid.org/0000-0001-7378-9194>

URL for web site:

• EDUCATION

2022-2025 PhD
Material Chemistry/ Department of Chemistry, Pavia University, Italy
Lorenzo Malavasi
2020 Master
Chemistry/ Department of Chemistry, Pavia University, Italy

• CURRENT POSITION(S)

2022 –2025 PhD student
Material Chemistry/ Department of Chemistry, Pavia University, Italy

• ORGANISATION OF SCIENTIFIC MEETINGS (if applicable)

2022 Poster contribute / MAT-SUS fall 2022 / Barcelona, Spain
2023 Oral contribute / ENERCHEM PhD school / Florence, Italy

Curriculum vitae (max. 3 pages)

PERSONAL INFORMATION

Family name, First name: Betti, Luca Angelo.

Researcher unique identifier (ORCID): 0009-0006-1537-7769

Date of birth:

• EDUCATION

2022 Master
Department of Chemistry, University of Pavia, Italy

• CURRENT POSITION(S)

2022 – On Going PhD Student
Department of Chemistry, University of Pavia, Italy
Supervisor: Prof. Lorenzo Malavasi

• PREVIOUS POSITIONS

2022 Research Grant
Department of Chemistry, University of Pavia, Italy
2021 Internship
Eni s.p.a., Novara, Italy

• FELLOWSHIPS AND AWARDS

2023 2nd FullProf School, ILL – Neutron for society, Grenoble, France
2017 Climathon, Associazione Cultura e Sviluppo, Alessandria, Italy

• SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS (if applicable)

2024 1 Master Student
Department of Chemistry, University of Pavia, Italy

• ORGANISATION OF SCIENTIFIC MEETINGS (if applicable)

2023 Poster contribute / 50th AIC Meeting/ Bologna, Italy
2023 Poster contribute / ENERCHEM PhD School/ Florence, Italy

• MEMBERSHIPS OF SCIENTIFIC SOCIETIES (if applicable)

2023 - 2024 Member, Research Network “*Associazione Cristallografi Italiani*”

- **MAJOR COLLABORATIONS (if applicable)**

Raffaella Biesuz, Chemometrics, Department of Chemistry, University of Pavia, Italy

Lisa Rita Magnaghi, Chemometrics, Department of Chemistry, University of Pavia, Italy

Curriculum vitae

PERSONAL INFORMATION

Family name, First name: Merlo, Francesca

Researcher unique identifiers: ORCID 0000-0003-1769-1760; Scopus Author ID 57200564914

Date of birth:

• EDUCATION

- 2021 PhD in Chemical and Pharmaceutical Sciences and Industrial Innovation
Department of Chemistry, University of Pavia, Italy
PhD Supervisor: Prof. Antonella Profumo
- 2017 Master in Chemistry (LM-54)
Department of Chemistry, University of Pavia, Italy

• CURRENT POSITION(S)

- 2023 – present Post-doc Fellow Researcher
Department of Chemistry, University of Pavia, Italy

• PREVIOUS POSITIONS

- 2022 – 2023 Post-doc Fellow Researcher
Department of Chemistry, University of Pavia, Italy
- 2020 – 2022 Post-doc Fellow Researcher
Department of Chemistry, University of Pavia, Italy

• FELLOWSHIPS AND AWARDS

- 2018 Award for Master's Thesis 2018, Italian Chemical Society - Division of Environmental
Chemistry and Cultural Heritage

• CO-SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS

- 2023 – 2024 1 Master Student
Department of Chemistry, University of Pavia, Italy
- 2022 – 2023 3 Master Students
Department of Chemistry, University of Pavia, Italy
- 2021 – 2022 1 Master Student
Department of Drug Science, University of Pavia, Italy
- 2020 – 2021 1 Master Student
Department of Chemistry, University of Pavia, Italy
- 2020 – 2021 1 Master Student
Department of Drug Science, University of Pavia, Italy

2018 – 2019 1 Master Student
Department of Chemistry, University of Pavia, Italy

• **REVIEWING ACTIVITIES**

2020–present Peer Reviewer for Talanta
2021–present Peer Reviewer, Journal of Hazardous Materials
2023–present Peer Reviewer, Science of Total Environment
2023–present Review Editor for Frontiers in Chemistry, section Analytical Chemistry

• **MEMBERSHIPS OF SCIENTIFIC SOCIETIES**

2018 – present Member, Società Chimica Italiana
2022 – present Member, EuChemS-DAC Sample Preparation Study Group and Network

• **MAJOR COLLABORATIONS**

- Prof. Maria Enriqueta Anticò and Prof. Claudia Fontàs, Development and application polymeric membrane for pollutants' enrichment, Department of Chemistry, University of Girona, Spain
- Prof. Enrica Calleri, Design and synthesis of polyHIPE material for analytical methods, Department of Drug Science, University of Pavia, Italy



TABELLA COSTI PERSONALE STANDARD				COSTO DEL PERSONALE	TD
FASCIA DI COSTO /LIVELLO	NUMERO SOGGETTI	COSTO ORARIO vedi nota	MONTE ORE		
Basso				- €	
Medio	1	48 €	369	17.712 €	
Alto	1	73 €	378	27.594 €	
TOTALI	2		747	45.306 €	

COSTO ORARIO: si deve far riferimento al Decreto Interministeriale n. 116 del 24/1/2018

Firma digitale del
Legale rappresentante del Proponente
 Università degli Studi di Pavia
 Il Rettore
 Prof. Francesco Svelto
(documento firmato digitalmente)



BUDGET DI PROGETTO	COSTO DEL PERSONALE	OVERHEAD	Costi per servizi di Consulenza Specialistica	Costi per licenze direttamente imputabili al progetto	Costi per materiali e attrezzature direttamente imputabili al progetto	Costi per altre tipologie di spese direttamente imputabili al progetto	COSTO TOTALE
Partecipante 1	45.306,00 €	6.795,90 €			67.898,10 €		120.000,00 €
Partecipante 2		0,00 €					0,00 €
Partecipante		0,00 €					0,00 €
Totale							120.000,00 €

Firma digitale del
Legale rappresentante del Proponente
 Università degli Studi di Pavia
 Il Rettore
 Prof. Francesco Svelto
(documento firmato digitalmente)