Politecnico di Bari

UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO

INTERUNIVERSITY PH.D. PROGRAM BETWEEN

POLITECNICO DI BARI AND UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO

IN INDUSTRY 4.0

Application of biopolymers to halide perovskite solar cells for flexible and robust devices

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Cycle

PhD in Industry 4.0 XXXVII cycle

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Description of the research program

The research activity is aimed to the development of advanced technologies in the field of photovoltaics (PV). In particular the realization of 3th generation solar cells, based on organometal halide perovskites / colloidal nanocrystals composites or organometal halide perovskites /organic molecules, integrated on conductive bio-based polymer substrate. Photovoltaic devices based on organic-inorganic hybrid perovskites have captured increasing attention in recent years because of their widely recognized advantages, such as promising power conversion efficiency (PCE), low cost and solution processibility[1]. The most efficient perovskites for photovoltaics have a 3D crystalline structure with a general formula ABX_3 (where A is a monovalent small cation such as methylammonium, Cs^+; B is a bivalent metal cation such as Pb^{2+} or Sn^{2+} and X is an halide, typically I^- or Br^-) and are used as active layer in PV that can be planar heterojunction type (p-i-n or n-i-p) or based on mesopouros scaffold. Among many, exceptional characteristics of hybrid halide perovskites, which cannot be found in conventional solution-processed semiconductors, are the long carrier diffusion length and carrier lifetimes, enabling a transport length larger than the depth of absorbed photons and high photovoltaic performance[2]. This class of materials is usually fabricated with either a one-step or a two-step process in solution. However, the surface morphology, nucleation rate and grain growth rate of the perovskite light absorber prepared by the solution reaction process are hard to control[3]. The research activity intends to develop controlled approaches to prepare perovskite absorbers for high-performance solar cells, the development of a new type of devices compatible with large-scale manufacturing and with characteristics of lightness and flexibility. The research will be divided into the following activities:

- *Synthesis of different hybrid perovskites* through the development and optimization of precursor solution and solvent engineering technology. Changing the organic cation, in particular perturbing size, can influence optical properties[4]. Making a mixture of organic cations or halides to improve optoelectronic properties[2,5]. An effort in the project will be the development of synthetic processes to obtain and to test a wide range of materials, among which the most promising system will be identified to be joined later in the composite for the development of photovoltaic devices.
- *Composites preparation and perovskite film formation.* Manipulation of defective grain boundaries in polycrystalline perovskite films is crucial to maximize both the optoelectronic properties and stability of the film and the corresponding devices[6].To overcome the defects at grain boundaries, to increase stability against harsh environmental stresses and to enhance all photovoltaic parameters, different additives will be tested, in order to obtain the absorber thin film with the best characteristics. The additives used, organic molecules or colloidal nanocrystals, which lead to the formation of composites will be chosen for their intrinsic properties, according to their functionalities and for the possible interactions with perovskite in the realization of the thin film of active material. For film growth, spin coating is a simple and very cheap technique. A balance and optimization between the relevant parameters for the deposition (such as solute concentration, solvent,..), will be achieved to obtain a good film quality of desired thickness and uniformity.
- *Characterization techniques of synthesized materials.* Morphological and Structural Analysis of the composite films can be obtained with scanning electron microscopy SEM, X-Ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy. The optical properties will also be studies by UV-VIS absorption and steady state and time resolved photoluminescence spectroscopy. In the case of hybrid perovskites, formed by self-assembly of precursor components dissolved in solvent, useful information can be obtained by the study of solutions with NMR spectroscopy.
- *Realization of a standard planar heterojunction perovskite solar cells.* The thin films obtained with mentioned above strategies, which showed the best features, can be tested as the photovoltaic active layer in the architecture of planar heterojunction solar cells on standard glass substrates (such as indium doped tin oxide). Different device architectures can be tested.
- *Realization of PHA-based growth substrates.* The replacement of glassy or metallic substrates with bio-based polymeric substrates, as support of solar cells, will be realized through solvent-casting. In this technique the PHAs pellets, supplied by a company, can be dissolved using different solvents, starting from those already mentioned in the literature[7,8] and testing new ones. The aim is to open new perspectives of design to realize perovskite solar cells with unprecedented improvement in device performance.
- *Functionalization of bio-based polymer substrates and flexible solar cell realization.* PHAs have never been used as support materials in solar cells. The effort of this research will be to work on the entire architecture of the device. Such substrates can be made conductive with the use of conductive oxides or graphene[9]. Further

effort will be focused on optimizing the synthetic methods of the conductive material, in order to obtain a support material that is also transparent with good mechanical properties.

- *Solar cell characterization.* In order to evaluate the performance of a solar cell, the current density—voltage (J–V) characteristics of the device will be measured and also the quantum efficiency measurements.

[1]Understanding the solvent-assisted crystallization mechanism inherent in efficient organic-inorganic halide perovskite solar cells. Dinghan Shen, Xiao Yu, Xin Cai, Ming Peng, Yingzhuang Ma, Xin Su, Lixin Xiao and Dechun Zou. The Royal Society of Chemistry **2012** DOI: 10.1039/x0xx00000x

[2]Methylammonium-formamidinium reactivity in aged organometal halide perovskite inks. Vitantonio Valenzano,Andrea Cesari,Federica Balzano, Antonella Milella, Francesco Fracassi, Andrea Listorti,Giuseppe Gigli,Aurora Rizzo, Gloria Uccello-Barretta and Silvia Colella. Cell Reports Physical Science.**2021** https://doi.org/10.1016/j.xcrp.2021.100432.

[3]Solid-state reaction process for high-quality organometallic halide perovskite thin film. Chien-Chung Hsu, Sheng-Min Yu, Kun-Mu Lee, Chuan-Jung Lin, Hao-Chien Cheng, Fu-Rong Chen. Elsevier **2021**.https://doi.org/10.1016/j.solmat.2021.111014

[4]The rapid evolution of highly efficient perovskite solar cells. Juan-Pablo Correa-Baena, Antonio Abate, Michael Saliba, Wolfgang Tress, T. Jesper Jacobsson, Michael Gra¨tzel and Anders Hagfeldt. The Royal Society of Chemistry **2017.** DOI: 10.1039/c6ee03397k

[5]Micrometer in an Organometal Trihalide Perovskite Absorber Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding. Science **2013.**DOI: 10.1126/science.1243982

[6]Perovskite-polymer composite cross-linker approach for highly-stable and efficient perovskitensolar cells. Tae-Hee Han, Jin-Wook Lee, Chungseok Choi, Shaun Tan, Changsoo Lee, Yepin Zhao, Zhenghong Dai, Nicholas De Marco, Sung-Joon Lee, Sang-Hoon Bae, Yonghai Yuan, Hyuck Mo Lee, Yu Huang, Yang Yang. Nature Communications **2019**. https://doi.org/10.1038/s41467-019-08455-z

[7]Preparation and Characterization of Films Based on a Natural P(3HB)/mcl-PHA Blend Obtained through the Co-culture of Cupriavidus Necator and Pseudomonas Citronellolis in Apple Pulp Waste. Ana Teresa Rebocho, João R. Pereira, Luisa A. Neves, Vítor D. Alves, Chantal Sevrin, Christian Grandfils, Filomena Freitas and Maria A. M. Reis. Bioengineering **2020**. doi:10.3390/bioengineering7020034

[8]Tuning the properties of polyhydroxybutyrate films using acetic acid via solvent casting. Preetam Anbukarasu, Dominic Sauvageau & Anastasia Elias. Scientific Reports,**2015**. DOI: 10.1038/srep17884

[9]The effects of solvent casting temperature and physical aging on polyhydroxybutyrate-graphene nanoplatelet composites. Preetam Anbukarasu, Dominic Sauvageau, Anastasia Elias. Polymer Composites. **2021**. DOI: 10.1002/pc.25915

Schedule of the research activities

First academic year

	Description	Period	Activity abroad
Insert name of first research activity	Synthesis of different hybrid perovskites through the development and optimization of precursor solution	01/2022-01/2023	NO
Insert name of second research activity	Composites preparation and perovskite film formation	01/2022-01/2023	NO
Insert name of third research activity	Realization of a standard planar heterojunction perovskite solar cells	01/2022-01/2023	NO

Second academic year

	Description	Period	Activity abroad
Insert name of first research activity	Realization of PHA-based growth substrates.	01/2023-01/2024	NO
Insert name of second research activity	Functionalization of bio-based polymer substrates	01/2023-01/2024	YES (places, times and details on the research activity to be defined)

Third academic year

	Description	Period	Activity abroad
Insert name of first research activity	Realization of flexible solar cells	01/2024-01/2025	NO
Insert name of second research activity	Solar cell characterization	01/2024-01/2025	NO

Provisional training and research activities plan

Specify with the related CFU (ECTS) the training activities that you plan to carry out or have completed in the three years (e.g., courses to attend, conferences, seminars, etc.). Please refer to the *Educational regulations of the Doctoral School of Politecnico di Bari*: http://www.poliba.it/sites/default/files/dottorati/regscudopoliba.pdf

Specify with the related CFU (ECTS) the research activities that you plan to carry out in the three years (e.g., individual research activity, supervision of students, integrative seminars to be given by the PhD student, activity of manuscript preparation for conferences or journals, activity of patents preparation, etc.).

First academic year

	Description	Period	Duration	CFU
PhD courses	Advanced materials for sensing technologies (SCuDO, Rosaria Picca)	12/2021-01/2022	10h	1
	Flexible and stretchable electronics (SCuDO, Francesco Dell'Olio)	02/2022	20h	2
	The post growth paradigm in planning research (SCuDO, Francesca Calace)	02/2022-03/2022	25h	2.5
	Innovative materials for energy conversion technologies (SCuDO, Andrea Listorti)	03/2022-04/2022	10h	1
	Multidisciplinary Research Applications of 3D Printing (SCuDo)	2022	20h	2
	Green photonics for a sustainable economy (SCuDO)	2022	20h	2
	Implementation and application of Design of Experiment techniques to experimental and numerical campaign (SCuDO)	2022	20h	2
	Laboratorio di inglese accademico (Scienze chimiche e molecolari)	2022	16h	1.6
	Soft chemistry for functional nanostructures (Scienze chimiche e molecolaru, Lucia Curri)	2022	16h	1.6
	Proprietà e caratterizzazione di materiali polimerici (Scienze chimiche e molecolari,Alfonso Maffezzoli)	2022	20h	2
Master's degree courses				

Participation to seminars and international congresses or workshops	Participation in specialized seminars	2022	5h	1.5
Presentation of research products at international congresses or workshops				
	TOTAL OF CFU FOR TRAINING ACTIVITIES			**19.2**
Individual research activity Students' supervision	Synthesis of different hybrid perovskites and composite preparation. Realization of a standard planar heterojunction perovskite solar cells.	2022	800h	32
Integrative didactive activities				
Preparation of manuscripts for conferences or journals	Preparation of articles regarding the research activity carried out and / or articles in review format, for publication in scientific journals	2022	220h	8.8
	TOTAL OF CFU FOR RESEARCH ACTIVITIES			
	TOTAL OF CFU FOR YEAR I			**60**

Second academic year

	Description	**Period**	**Duration**	**CFU**
PhD courses				
Master's degree courses				
Participation to seminars and international congresses or workshops	Participation in specialized seminars	2023	16h	4.8
	Participation in specialized seminars	2023	3h e 30 min	1
Presentation of research	Presentation of a research product at an international congress or conference	2023		2

products at international congresses or workshops				
	TOTAL OF CFU FOR TRAINING ACTIVITIES			**7.8**
Individual research activity	Realization of PHA-based growth substrates and Functionalization of the best substrated to make them conductive. For this last task, activities abroad are expected.	2023	1000h	40
Students' supervision				
Integrative didactive activities				
Preparation of manuscripts for conferences or journals	Preparation of articles regarding the research activity carried out and / or articles in review format, for publication in scientific journals	2023	305h	12.2
	TOTAL OF CFU FOR RESEARCH ACTIVITIES			
	TOTAL OF CFU FOR YEAR II			**60**

Third academic year

	Description	**Period**	**Duration**	**CFU**
PhD courses	Chimica e tutela della salute e dell'ambiente: dai regolamenti REACH e CLP alla Life Cycle Assessment (Scienze chimiche e molecolari, Vincenzo DeLeo)	2024	16h	1.6
	Watching nanomaterials with X-ray eyes: the power of X-ray diffraction with incoherent and coherent beams (Scienze chimiche e molecolari, Dott.ssa Giannini)	2024	16h	1.6
	XPS as a powerful tool for surfaces and nanomaterials characterization (Scienze chimiche e molecolari, Dott.ssa Nicoletta Ditaranto)	2024	16h	1.6
	Sintesi Organiche Eco-compatibili (Scienze chimiche e molecolari, Dott.Cotugno)	2024	16h	1.6
	Cenni di Operazioni unitarie, fenomeni di trasporto e reattori chimici (Scienze chimiche e molecolari, Federico Cangialosi)	2024	16h	1.6
Master's degree courses				
Participation to seminars and international congresses or workshops	Participation in specialized seminars	2024	8h	2.4
	Participation in specialized seminars	2024	5h 30min	1.6

Presentation of research products at international congresses or workshops				
	TOTAL OF CFU FOR TRAINING ACTIVITIES			**12**
Individual research activity	Enhancement of the performance of active materials. Realization of a flexible and light solar cell. Characterization techniques.	2024	900h	36
Students' supervision				
Integrative didactive activities				
Preparation of manuscripts for conferences or journals	Preparation of one or more manuscripts for a scientific journal, as a research product of the new experimental activity carried out and of the final paper of the research thesis	2024	300h	12
	TOTAL OF CFU FOR RESEARCH ACTIVITIES			
	TOTAL OF CFU FOR YEAR III			**60**
	TOTAL OF CFU FOR THE WHOLE PHD COURSE			**180**