

Master in Molecular Nanoscience and Nanotechnology

Master dissertation defense

July 24th, 2024. SS6 Seminar

Confidential

9:30 Emilie Eustache

HfZrO Atomic Layer Deposition and characterization for MIM and ferroelectric memories applications

Public

10:00 María Tamayo Fraile

Ultrastable Pyrazolate Porphyrin Metal-Organic Frameworks for Environmentally Relevant Applications

10:30 Marc López Molla

Exploring chemical byways towards pnictogens-based heterostructures

11:00 Tamara Donate Rivas

Perovskite Silicon Tandem Solar Cells



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STMicroelectronics

HfZrO Atomic Layer Deposition and characterization for MIM and ferroelectric memories applications

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19/02/24 – 19/08/24

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Master's Thesis

Ultrastable Pyrazolate Porphyrin Metal-Organic Frameworks for Environmentally Relevant Applications

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Master of Molecular Nanoscience and Nanotechnology
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ABSTRACT

Nowadays there is an environmental crisis caused by global warming and greenhouse effect which has triggered huge problems such as extreme weather, extinction of species, acidification of the oceans, etc. More specifically, carbon dioxide (CO₂) is one of the most relevant greenhouse gases due to the severe increase in its atmospheric concentration in recent years. Despite various approaches have been proposed to convert CO₂ to value-added products, the electrocatalytic CO₂ reduction reaction (eCO₂RR) is assessed as one of the most promising conversions pathways.

Recently, metal-organic frameworks (MOFs) have been considered as plausible and attractive alternative heterogeneous electrocatalysts. Additionally, the use high-catalytic-activity metalloporphyrin linkers as MOF building blocks provides a promising tunable platform to carry out a wide variety of reactions such as eCO₂RR. Nevertheless, MOFs stability under carbonate alkaline electrocatalytic conditions, as the ones used in eCO₂RR, remains a significant challenge, especially for prototypical carboxylate-based porphyrin MOFs. Conversely, MOFs featuring pyrazolate-porphyrin (pz-P) linkers could offer enhanced chemical stability for reactions requiring specially demanding conditions such as eCO₂RR. However, their use in such applications is still marginal compared to carboxylate MOFs.

The present Master Thesis, aims to synthesize a series of pyrazole-porphyrin MOFs, based on the previously reported PCN-601 [Ni₈(OH)₄(H₂O)₂(NiTPP)₃], but with varying metalloporphyrin units (PCN-601-M). Notably, the starting H₄TPP (5,10,15,20-tetra(1H-pyrazol-4-yl)-porphyrin) is transformed to NiTTP during the synthesis. In order to finely control metal content in PCN-601-M several MTPP (M = Ni, Co, Cu) have been synthesized from the commercial H₄TPP and using different pyrazol protective groups (PG: Boc and Tr) to ensure the inclusion of the metal into the active site of the porphyrin. Therefore, the results obtained in this project will allow to successfully control metal incorporation into PCN-601-M for the first time.

The synthesis of the originally reported PCN-601-Ni has been optimized after finding reproducibility issues in its published synthesis protocol. These have been overcome to obtain a robust experimental procedure. The materials obtained have been characterized using Powder X-Ray Diffraction (PXRD), N₂ physisorption, Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA). Moreover, PCN-601-Ni has been subjected to stability tests in a alkaline carbonate electrolyte, as the one used in eCO₂RR, for the first time. Thus, confirming its stability in such conditions and their potential as a robust catalyst for CO₂ conversion.

Besides the synthesis of PCN-601-Ni from H₄TTP, we have attempted its synthesis from PG-TTP (PG = Tr, Boc). Despite the expected improvement on textural properties has not been found in the case of Boc protecting group, in the case of Tr, a new crystalline phase has been obtained, that we tentatively assigned to a new pz-P MOF with a topology different from that of PCN-601 (*ftw*), the only pz-P MOF reported up to date.

MASTER'S THESIS

MASTER IN MOLECULAR NANOSCIENCE AND NANOTECHNOLOGY

2023 – 2024



VNIVERSITAT DE VALÈNCIA

Exploring chemical byways towards pnictogens-based heterostructures

Marc López Molla

Supervised by Dr. Matteo Andrea Lucherelli & Dr. Gonzalo Abellán Sáez

July 2024

SUMMARY

Interdisciplinary research in materials science has developed new approaches to combine different classes of materials, aiming to obtain unique hybrid heterostructures with enhanced properties. This work seeks to explore the synthesis of hybrid heterostructures based on C₆₀ fullerenes and 2D pnictogens, creating materials with advanced functionalities. To achieve this, it focuses on the functionalization of fullerenes with specific groups and the manipulation of 2D bismuth at the nanometric scale.

During the thesis, two main areas were investigated: the functionalization of C₆₀ fullerene and 2D bismuth. Regarding fullerenes, the aim was to obtain derivatives with diazonium salt and thiol groups to form covalent bonds with bismuth. For bismuth, 2D bismuth nanosheets (BiNSs) were synthesized and its properties were confirmed using Raman spectroscopy and XPS analysis, among others. Additionally, two functionalization reactions were explored using 4-fluorobenzenethiol and diazonium salt derivatives of 4-aminobenzoic acid.

Overall, significant progress was made in understanding the reactivity of bismuth nanomaterials and fullerenes' functionalization. Preliminary results indicate the potential for creating 2D-Bi@C₆₀ hybrid heterostructures, warranting further investigation in the coming years.



VNIVERSITAT DE VALÈNCIA



Master Thesis

Master in Molecular Science and Nanotechnology

Perovskite Silicon Tandem Solar Cells

Tamara Donate Rivas

Directed by:

Hendrik J. Bolink

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Abstract

In recent years, perovskite solar cells have been increasingly developed due to their promising properties for photovoltaics. Although silicon remains dominant in the solar cell industry, combining perovskite and silicon in tandem solar cells can surpass the limitations of single junction cells set by the Shockley-Queisser limit. Tandem solar cells offer the best of both materials potentially achieving higher power conversion efficiencies. To optimize these devices, it is crucial to understand the individual performance of each cell under combined behaviour. This project investigates the effect the bottom cell textured surface has on the properties of the perovskite top cell. We do this by comparing the properties of tandem cells with those of single junction perovskite cells deposited on textured conductive substrates.

Resumen

En los últimos años, las células solares de perovskita se han desarrollado cada vez más debido a sus propiedades prometedoras para el campo de la fotovoltaica. Aunque el silicio sigue siendo dominante en la industria de las células solares, la combinación de perovskita y silicio en células solares en tándem puede superar las limitaciones de las células de unión simple establecidas por el límite de Shockley-Queisser. Las células solares en tándem ofrecen lo mejor de ambos materiales, potencialmente logrando mayores eficiencias de conversión de potencia. Para optimizar estos dispositivos, es crucial comprender el rendimiento individual de cada célula bajo comportamiento combinado. Este proyecto investiga el efecto que tiene la superficie texturizada de la célula inferior en las propiedades de la célula superior de perovskita. Esto lo hacemos comparando las propiedades de las células en tándem con las de las células de perovskita de unión simple depositadas en sustratos conductores texturizados.