nffa.eu

PILOT 2021 2026

DELIVERABLE REPORT

WP15 JA5 - Correlative Nano-Spectroscopy and Nano-Diffraction

D15.1
Design of platforms for liquid cells

Due date

M12

This initiative has received funding from the EU's H2020 framework program
for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

PROJECT DETAILS

PROJECT ACRONYM	PROJECT TITLE
NEP	Nanoscience Foundries and Fine Analysis - Europe|PILOT

GRANT AGREEMENT NO:	FUNDING SCHEME
101007417	RIA - Research and Innovation Action

START DATE

01/03/2021

WORK PACKAGE DETAILS

WORK PACKAGE ID	WORK PACKAGE TITLE
WP15	JA5-Correlative Nano-Spectroscopy and Nano-Diffraction

WORK PACKAGE LEADER

Dr. Thomas Keller (DESY)

DELIVERABLE DETAILS

DELIVERABLE ID	DELIVERABLE TITLE
D15.1	Design of platforms for liquid cells

DELIVERABLE DESCRIPTION

Technical specifications for the design of the liquid/gas cells are described based on target experiments and the requirements from the X-ray end stations. The first prototypes and preliminary tests are described.

DUE DATE	ACTUAL SUBMISSION DATE
M12 28/02/2022	01/03/2022

AUTHORS

Jordi Fraxedas (ICN2), Francesc Perez-Murano (CSIC)

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

PERSON RESPONSIBLE FOR THE DELIVERABLE

Prof. Francesc Perez-Murano (CSIC)

NATURE

☒ R - Report

☐ P - Prototype

☐ DEC - Websites, Patent filing, Press & media actions, Videos, etc

☐ O - Other

DISSEMINATION LEVEL

☒ P - Public

☐ PP - Restricted to other programme participants & EC: (Specify)

☐ RE - Restricted to a group (Specify)

☐ CO - Confidential, only for members of the consortium

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

REPORT **DETAILS**

ACTUAL SUBMISSION DATE	NUMBER OF PAGES
01/03/2022	14

FOR MORE INFO PLEASE CONTACT

Francesc Perez-Murano,
IMB-CNM, CSIC
Campus UAB. 08193 Bellaterra.
Spain

email:Francesc.Perez@csic.es

VERSION	DATE	AUTHOR(S)	DESCRIPTION / REASON FOR MODIFICATION	STATUS
1	23/02/2022	Francesc Perez-Murano/ Jordi Fraxedas	First Draft	Draft
2	23/02/2022	Thomas F. Keller	Approval by working package leader	Approved
3	25/02/2022	Elisabetta Narducci	Formal checking	Minor Revisions
4	01/03/2022	Emmanuel Stratakis	Approval and minor changes	Final
				Choose an item.
				Choose an item.
				Choose an item.

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

CONTENTS

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

INTRODUCTION

Workpackage JA5- Correlative Nano-Spectroscopy and Nano-Diffraction aims to establish a user platform for routine experiments at Nanolabs and analytical large-scale facilities (ALSFs) permitting to collect structural and chemical information from a statistically relevant number of distinct nanoscale objects.

One of the objectives of JA5 is to provide dedicated sample environments to investigate the dynamical behaviour of nanoscale objects *in situ* during e.g., catalytic, electrochemical or corrosion experiments in liquid or gaseous environments.

In view of this objective, task 15.3 (Sample environments for in situ correlative analysis) centralizes the work for the design, test and offer of a dedicated micro/nano fabrication platform for in situ sample environment.

The present deliverable summarizes the efforts carried out during the first 12 months of the project towards the realization of the micro/nano fabricated platform. It includes the following aspects:

- The definition of target experiments that will serve as demonstrators of the scientific interest of the platform.
- The design and realization first prototype of a liquid cell for initial validation experiments
- The design and realization of membrane-containing microchips to be incorporated into the platform
- An outlook of next steps to be addressed in task 15.3

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

TARGET EXPERIMENTS

As a scientific objective to drive the design and realization of the platform for measurements in specific environments, the investigation of the mechanisms responsible for the self-sustained motion of nano-objects (nanomotors) in water has been selected for their relevance in water remediation. See e.g.; ACS Appl. Mater. Interfaces, 2017, 9, 44948–44953; Acc. Chem. Res., 2018, 51, 1921–1930; J. Synchrotron Rad 2019, 26, 1288-1293; Soft Matter, 2020, 16, 3717-3726.

The exploration of efficient strategies to purify water becomes increasingly urgent due to the growing demand in water consumption. One of the emerging strategies uses nanomotors whose motion in water is induced by self-generated physicochemical gradients (see figure 1). The nanomotors move by chemical gradients induced from light-activated water redox reactions at their surfaces, which generate at the same time reactive oxygen species that fuel the contaminant degradation. We propose to characterize the water/solid interfaces of different metal/semiconductor nanomotors by means of HAXPES experiments in the liquid state and in operando conditions (under illumination with white light) using a dispersion of nanomotors in a liquid cell designed for the experiments hosting microfabricated thin Si3N4 membranes. HAXPES is needed in order to provide sufficient high kinetic energies to the photoelectrons in order to overcome the water/membrane barrier in their way to the analyser and in order to reduce water radiolysis. Previous near ambient pressure XPS performed on catalytic pumps, the immobilized motor counterparts, have shown that the noble metal films are reduced by the combined effect of an intense soft X-ray photon beam and condensed water due to water radiolysis, hindering the analysis of the oxidation/reduction processes [J. Synchrotron Rad 2019, 26, 1288-1293].

In the future, the platform could also be used to characterize other nano-objects such as nanoparticles and biomolecules in water at different salt contents.

A first cell prototype will contain a dispersion of nanomotors in water without circulation and the motion will be generated by external illumination with white light. In a second stage the liquid will circulate within the cell volume. The cell will be sealed with a silicon chip containing a thin membrane (either Si3N4 or graphene/Si3N4) that will allow photon-in/electrons-out experiments. Special attention will be devoted to UHV compatibility, membrane robustness and surface charging. The work will be performed in collaboration with Dr. Jean-Pascal Rueff's team at SOLEIL. The cell will be designed to be used at the HAXPES end station at the GALAXIES beamline at SOLEIL.

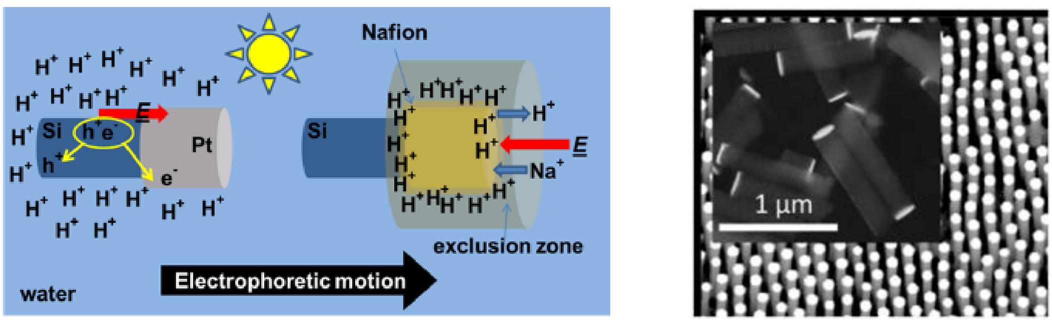

Figure 1: (left) scheme of the electro- and diffusio-phoretic mechanisms in Pt/Si and Si/Nafion nanomotors and (right) SEM image of Pt/Si nanomotors.

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

LIQUID CELL SPECIFICATIONS AND DESIGN

Liquid cell specifications

It has been decided to build a liquid cell to be used at the HAXPES end station at the GALAXIES beam line at SOLEIL. Besides the obvious reason that it is possible to perform HAXPES measurements at GALAXIES, another reason for this selection is the running activity in SOLEIL on performing 'in situ' measurements in liquid.

The first prototype of the liquid cell will be aimed to:

- Test membrane integrity in vacuum (off-line)
- First measurements at HAXPES endstation (dispersion of Au NPs in water may be used as a test sample before exploring the Au and Pt/Si nanomotors)
- Static (non circulating) liquid. Liquid flow at a later stage
- Undesirable formation of bubbles due to water radiolysis induced by the X-ray beam must be taken into account. This effect should be reduced using high-energy photons.
- Liquid must be illuminated with white light during the experiments. Options:
    - From the front through the membrane with external light source and some optics for focusing
    - From the front through the membrane bringing light to the chamber with an optical fiber
    - To be also explored: Transparent liquid cell material (glass) or additional aperture in the liquid cell to bring light into the cell
- Materials for the liquid cell: Aluminium and/or stainless steel
- Electrical contact to the cell for electrical discharge of the membrane
- Incidence angle will be very low for HAXPES (5º).

This first prototype will be later on adapted for dynamic measurements (circulating liquids) based on the dynamic liquid cell that exists at the LUCIA beam line cell in SOLEIL. Circulating fluidic will deserve a minimum quantity of liquid. Probably 5-10 ml will be needed. Adaptations need at GALAXIES will be evaluated (optical microscope, manipulator, …).

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

Liquid cell design

The design of the first prototype of the liquid cell has been based on the well-known and extensively used OMICRON sample holder plates and an existing liquid cell prototype design for GALAXIES at SOLEIL (see figure 2).

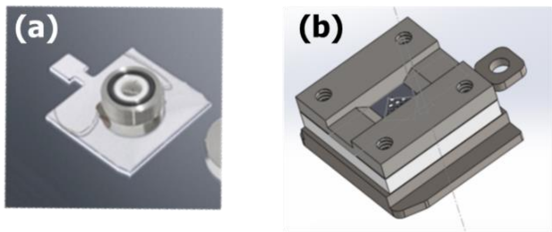

Figure 2: (a) Commercial liquid cell from SPECS GmbH for electrochemical experiments and (b) prototype of liquid cell for HAXPES at GALAXIES designed by F. Capone & J. Sottmann.

An alternative design developed at ICN2 and IMB-CNM-CSIC is shown below (Figure 3). A beaker, which will contain the liquid, is directly machined on an Omicron-type plate and sealed with a cover plate that contains an orifice on the centre where 2 mm x 2 mm silicon chips will be glued with UHV conducting epoxy. Two lateral tapped holes permit the injection of liquid and elimination of bubbles. Vacuum sealing is achieved with small Viton O-rings.

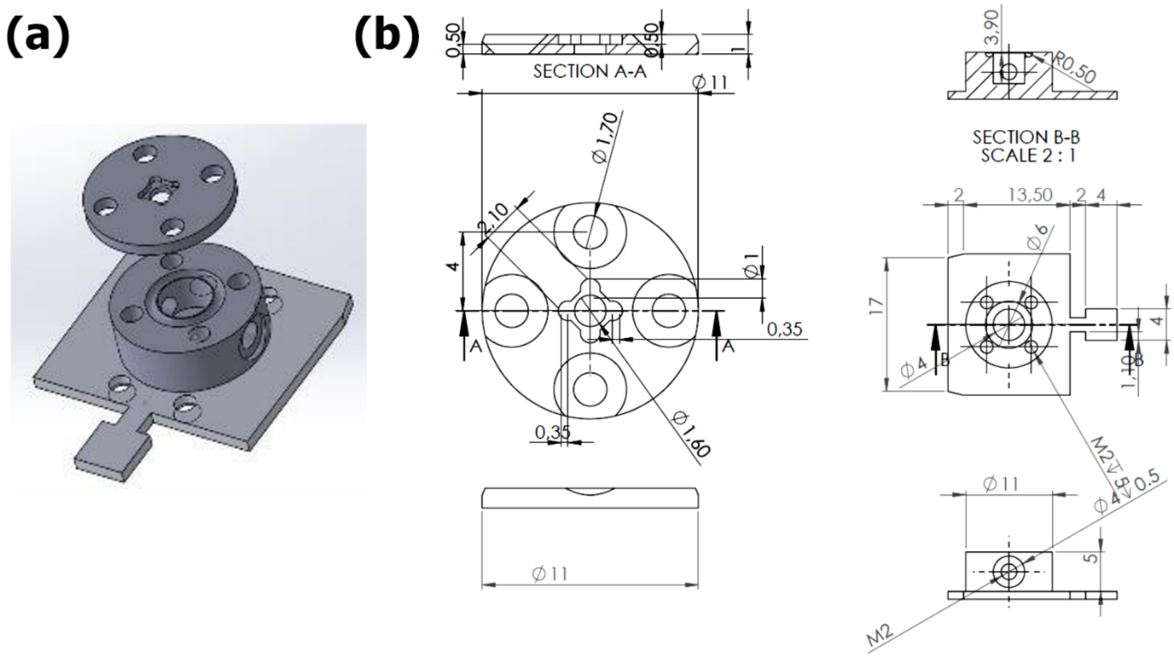

Figure 3: Design of the first ICN2-CNM prototype of liquid cell (dimensions are in mm)

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

First prototype of liquid cell

A first prototype of the liquid cell has been fabricated, according to the design reported in Figure 4.

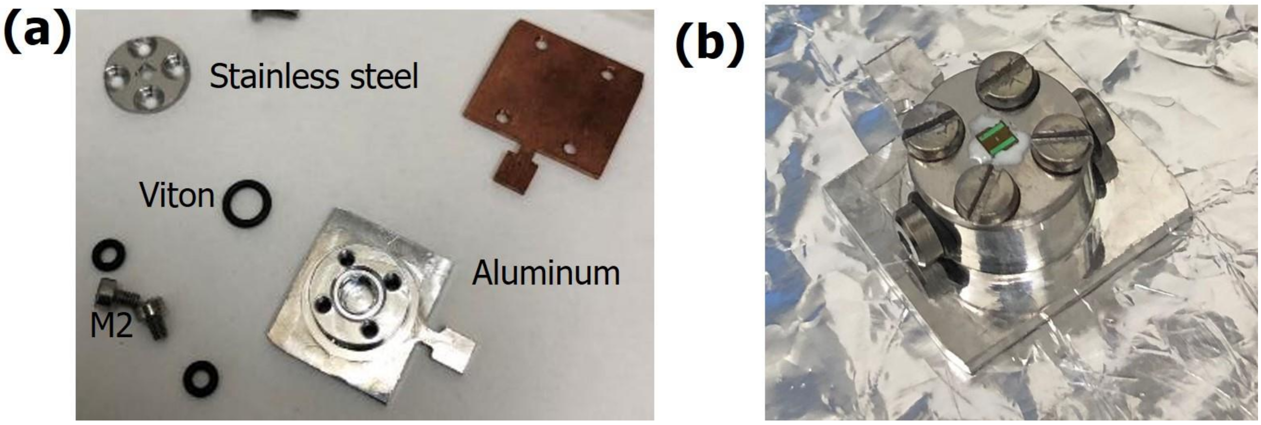

Figure 4: Photographs of the first prototype of the liquid cell. (a) The liquid cell with the different parts before assembly. (b) The liquid cell mounted where a microfabricated chip supporting a Si3N4 membrane has been glued.

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

MEMBRANE CHIPS SPECIFICATIONS AND DESIGN

Membrane chips specifications

The definition of the specifications for the membrane chips to fulfil with the target experimental requirements have been obtained after several discussions with SOLEIL's staff. Main specifications are summarized below:

- A commercial reference for the chips with membranes are those from SILSON: https://www.silson.com/product/silicon-nitride-membranes/
- The chip framework is to be made of 500 μm thick silicon
- Use of OMICRON-type sample holders requires a chip size of 10 mm x 10 mm (dynamic measurements)
- Membrane size: 500 μm x 30 μm would be sufficient given the actual dimensions of the beam (100 um (H) x 30 um (V). Modelling and evaluation is needed to further fine tune membrane dimensions.
- Materials for the membrane: Low stress silicon nitride (thickness 25 nm – 50 nm). In a second stage, actions to increase the robustness of the membrane will be considered, as for example the uses of thicker silicon nitride (200 nm) membranes with microfabricated holes coated with graphene (like in Velasco-Velez JJ, doi.org/10.1002/anie.201506044)
- It may be necessary to include conductive electrodes to be located close to the membrane to avoid electrical charging from X-ray illumination
- Main liquid to be employed will be water. The use of other liquids and solvents will not be considered for the moment.
- Chips with membranes will have to be tested in vacuum and exposed to x-ray irradiation to analyze fragility and durability before used in real experiments.

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

Membrane chip prototype microfabrication

The fabrication of chips with membranes have been realized at IMB-CNM. The fabrication process relies on a pre-existing technology at IMB-CNM. The aim of the fabrication of the first prototypes of membrane chips is to test the endurance of the membranes. For this reason, a batch of chips with three different thicknesses of Si3N4 (100 nm, 50 nm and 25 nm) have been fabricated. Figure 5 shows photographs of the wafers before releasing the chips (Figure 5.a), photographs of some of the chips (Figure 5.b) and SEM images of the chips and membranes (Figure 5.c).

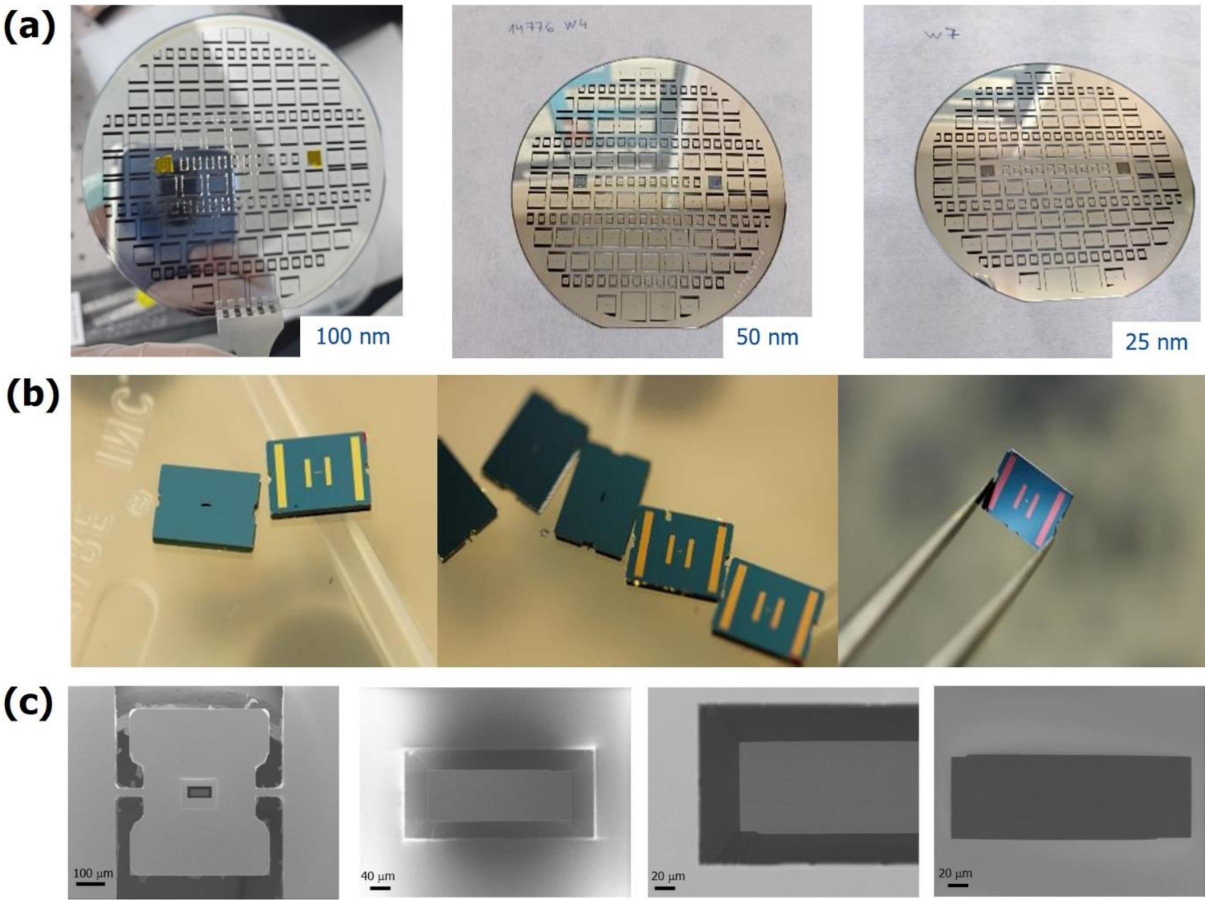

Figure 5: Images of the first prototypes of the membrane chips. (a) Photographs of three fabricated wafers before releasing the chips. Multiple designs are included in the wafers. The silicon nitride membrane thickness of each wafer is depicted in each photograph. (b) Optical images of some of the chips after being released from the wafer. (c) SEM images of the chips and membranes.

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

Tests of membrane chips

Preliminary tests of the fabricated membrane chips are currently being performed to check that the integrity of the membrane remains under sustaining a differential pressure (air/ vacuum and liquid / vacuum).

First tests were performed by using an atomic force microscope (AFM) (ICON system, Bruker), where the difference of pressure is originated from the vacuum chuck (see figure 6 (a)). AFM images taken in tapping mode reveal the deformation induced on the membrane by the difference of pressure. The membrane deformation has been modelled using the methodology described in *O. Tabata et al, Sensors and Actuators 20, 135-141 (1989).* The level of deformation observed is consistent with a build-in tensile stress of the membrane of 500 MPa.

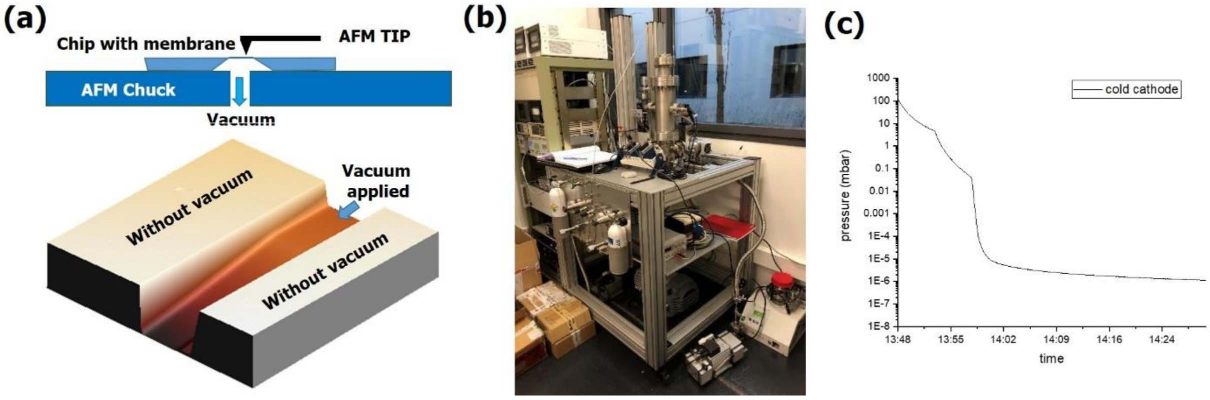

Figure 6: Tests of the integrity of the membranes with the microfabricated chips. (a) AFM tests in low vacuum to characterize the amount of membrane deflection. (b-c) Tests in a high vacuum chamber (down to $5 \cdot 10^{-8}$ mbar, chamber shown in (b) to determine membrane impermeability.

Additional tests have been performed under high vacuum using the liquid cell shown in figure 4. The liquid cell was filled with MilliQ water; microfabricated chips were glued to the cover piece with UHV compatible epoxy and introduced in the vacuum chamber. Pumping was performed in three consecutive stages: through a needle valve and a membrane pump (down to 10 mbar), with a dry scroll pump (down to 10^{-2} mbar) and finally with a turbomolecular pump. The first test has been performed with 100 and 50 nm thick membranes, and it demonstrated the impermeability of the membrane, as pressures of $5 \cdot 10^{-8}$ mbar were achieved after 24 hours (base pressure of the system without bakeout).

This initiative has received funding from the EU's H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project

CONCLUSIONS AND OUTLOOK

This deliverable reports the specifications and design of the liquid cell and microfabricated chips with membranes to be part of the micro/nano fabricated platforms to perform measurements in liquid cells. The specifications have been defined according to a specific target experiment (investigation of light activated water redox reactions at the metal and semiconductor surfaces of nanomotors) and having the GALAXIES beam line at SOLEIL as the reference for HAXPES measurements.

First prototypes of the liquid cells and membrane chips have been fabricated and preliminary test measurements have been performed, which shows the feasibility for measurements in liquid under vacuum conditions.

During the next months, the liquid cell will be optimized and a second generation of chips will be fabricated with the appropriate dimensions for both GALAXIES static and dynamic liquid cells.

An application for beam time at SOLEIL has been submitted (February 2020, title: “Motile noble metal based photocatalytic nanomotors for water remediation”), which will provide the opportunity to check the performance of the platform under real conditions. In case of acceptance of the proposal, experiments will be tentatively performed from October 2022 (M20).

Overall, task 15.3 is running as expected and no major problems are to be reported, and we expect to fulfil the Milestone “Fabricated and tested liquid cells for X-ray nano-spectroscopy” in M24.

This initiative has received funding from the EU’s H2020 framework program for research and innovation under grant agreement n. 101007417, NFFA-Europe Pilot Project