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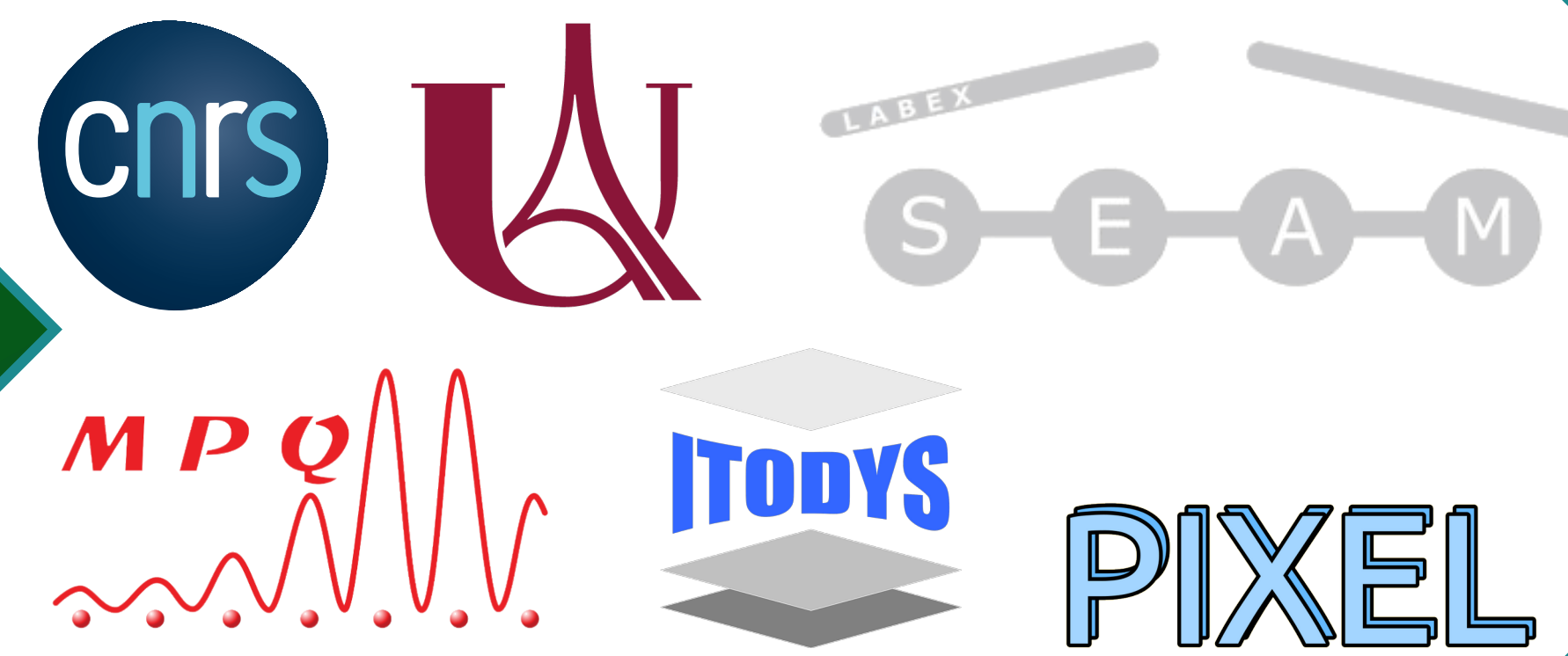
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# Building a comprehensive platform for the synthesis, assessment of electrocatalytic activity and property tuning of high-entropy nano-alloys



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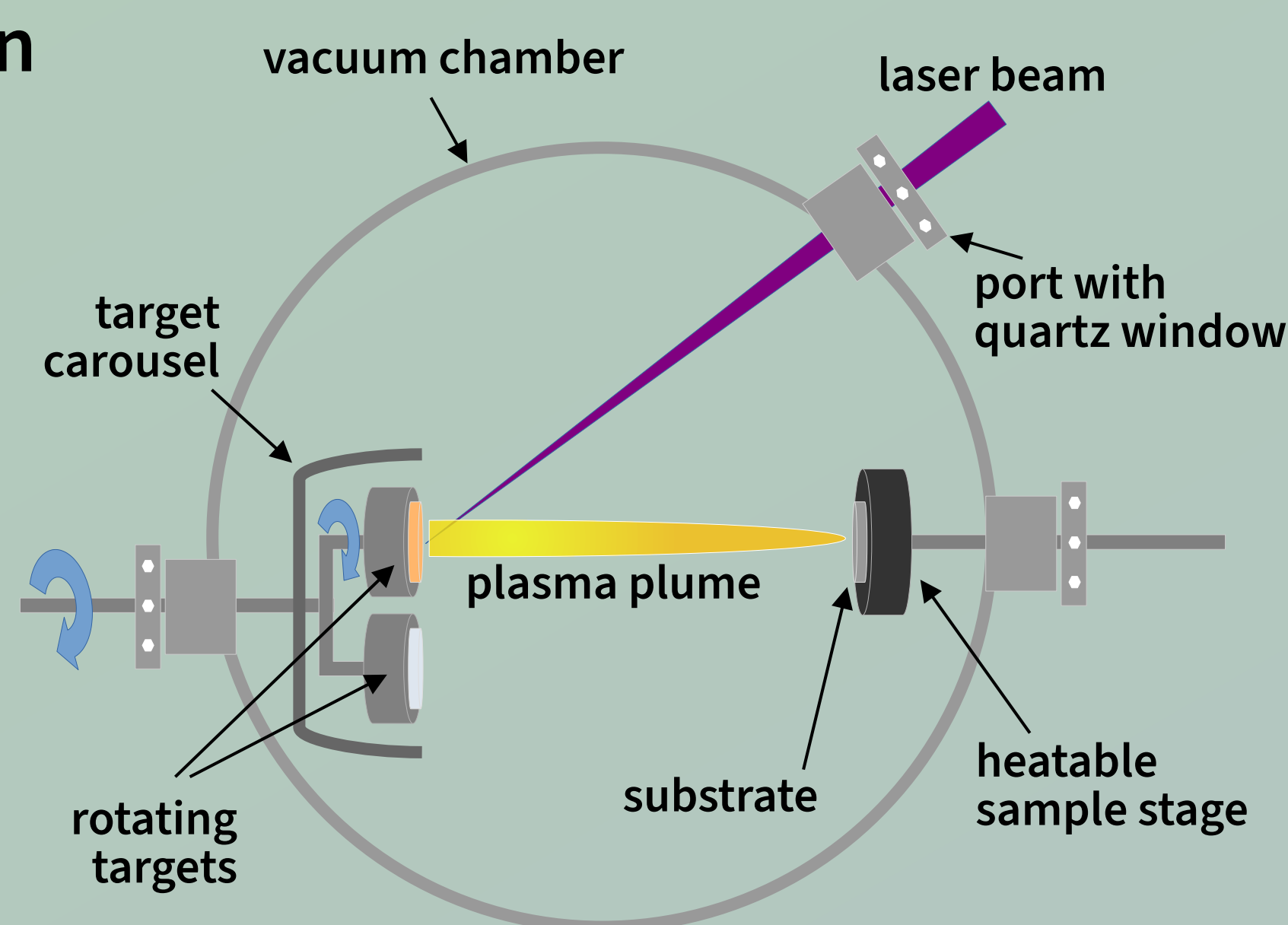
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## Probing the secrets of high-entropy nano-alloy electrocatalysts

High-entropy nano-alloys (HENA) constitute a new family of compounds with very promising physical, chemical, mechanical, electrical, etc., properties. Touted as the Swiss Army knife of materials, given their multiple constituent metals (5 or more) and their so-called “cocktail effect”, they make very attractive candidates for catalytic and electrocatalytic applications. This joint project aims to synthesize HENAs by physical means, and then to study operando their electrocatalytic properties at the single-object level. Because the targeted materials are nanostructured and composed of multiple elements, state-of-the-art analytical methodologies will be used to characterize their chemical and structural properties before, during and after the reaction. The project will focus in particular on their reactivity and long-term stability with respect to the hydrogen evolution reaction (HER) and CO<sub>2</sub> reduction (CO<sub>2</sub>RR). Our team (MEANS) has an expertise in the synthesis of HENAs, as well as their characterization *ex situ* and *operando* via transmission electron microscopy (TEM) and related techniques (electron diffraction, energy-dispersive and electron energy loss spectroscopies), while electrochemical TEM (EC-TEM) is being heavily developed. Information about the long-term stability of HENAs and the reaction environment in actual operating conditions can be gleaned through interferometric scattering microscopy (iSCAT) coupled to electroanalytical techniques, a powerful tool evolved by our collaborators in the PIXEL team. A multi-scale, multi-technique approach is being put together, combining iSCAT and TEM, both coupled with electrochemistry. Insights gained through these means will be then used to guide the compositional tuning of HENAs, with regard to the desired properties (catalytic activity, corrosion resistance, etc.).

### 1. Pulsed laser deposition

Pulsed laser deposition is a physical vapor deposition technique, where a (pulsed) laser beam is focused on a target of the material to be deposited, inside a vacuum chamber. The material is ablated, forming a plasma plume perpendicular to the surface of the target, which expands towards the substrate onto which it is deposited; initially as scattered atoms and clusters of atoms and gradually growing into a film. By controlling the conditions of deposition as well as the time, it is possible to obtain homogeneous nanoparticles. This technique also allows the fabrication of alloys, which are impossible to manufacture through conventional means for thermodynamic reasons. The main components of a PLD setup are shown in the figure on the right.



### 2. Initial electrochemical assessment

Because of the complex nature of HENAs, it is difficult to foresee their electrocatalytic behavior or any stability issues. For this reason, they will be characterized by linear sweep voltammetry (LSV) with conditions close to HER electrolyzers using the scanning droplet cell technique. This strategy will be useful in probing each sample in a different region of interest to assess substrate homogeneity and measurement reproducibility. Complemented by *ex-situ* SEM/TEM/IR analyses run inside the micro-EC cells defined by the microdroplets, the geometry of the NPs and, consequently, the electroactive surface will be determined. This approach, will be essential for a reliable comparison of the electrocatalytic properties of the HENAs.

The Tafel analysis of the data will then be used for drawing Volcano plots of HER efficiency as function of HENAs elemental composition. Finally, the time-dependent catalytic stability will be measured by galvanostatic experiments and by recording potential fluctuation using the same strategy described above.

The methodology will then be extended to study CO<sub>2</sub>RR considering the superior chemical complexity in its electrocatalytic mechanism.

### 4. Conclusions

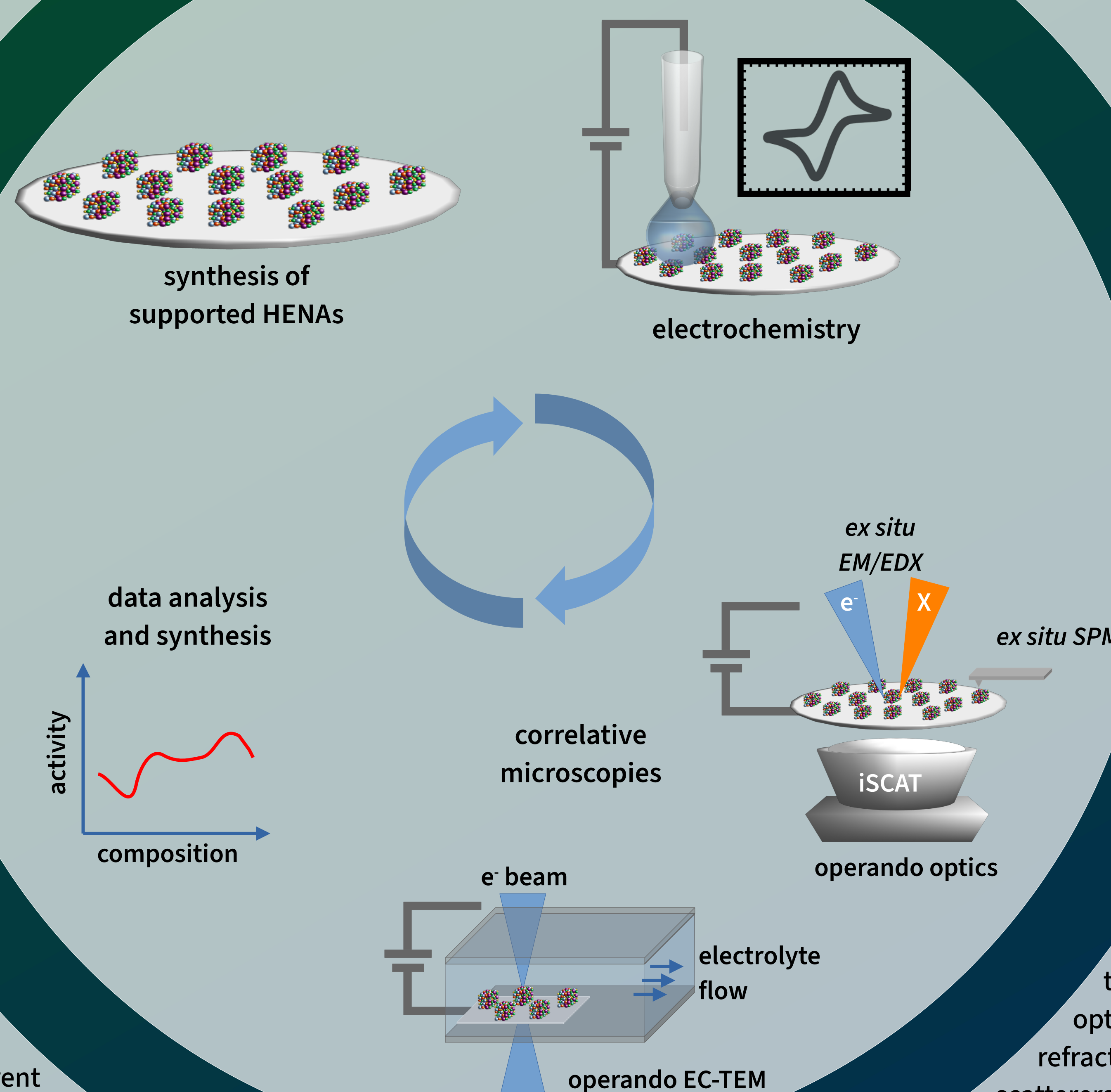
The wealth of data accumulated in the previous stages should be sufficient to shed light on the catalytic mechanism and the degradation processes – if any.

With the ability to monitor individual particles before, during and after the reaction, structural, morphological and compositional changes should be immediately apparent.

Armed with that information, we hope to be in a position to better understand the interplay between all the different constituents of the HENAs, so as to rationally adapt their composition to specific systems, enhancing their activity and promoting their chemical stability.

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### 3. Degradation studies

Interferometric scattering microscopy operates on the principle of the interference between the light scattered by a NP and the light reflected by a conductive transparent substrate used as a working electrode. The iSCAT technique can detect very small NPs (down to 3 nm in diameter) as the optical signal is proportional to the NP volume (the methodology is often called optical mass spectrometry) and is highly sensitive to refractive index changes (chemical composition) of the scatterers.

Therefore, iSCAT appears ideal for monitoring at high temporal resolution (up to kHz) and for long periods of time, the restructuring and/or the dissolution (optical mass spectrometry) of single NPs. In addition, the wide field of view (> 50x50 μm<sup>2</sup>) imaging allows to probe the behavior of many (> 1k) NPs within a large ensemble of them to produce statistically relevant results.

Electrochemical TEM (EC-TEM), enables the direct observation of the surface of an electron-transparent microelectrode with nanometric resolution while allowing the simultaneous measurement of the electrochemical response. Operando EC-TEM studies will be conducted based on the best materials and electrochemical conditions determined in the previous stages. This step will enhance our comprehension of any degradation processes highlighted by the *ex-situ* studies. It will permit to deconvolute reaction mechanisms and help in the elucidation of key parameters dominating the activity and selectivity. This is particularly important in the case of more complex reactions like the CO<sub>2</sub>RR. Finally, operando observations will bring direct insight into the main expected degradation processes such as elemental leaching or surface segregation processes occurring during the reactions.