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The Potentiality of Optics in Correlative Microscopies Strategies for *In situ* Nanoscale Probing of Electrochemical Processes

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Electrocatalysis holds the promise of producing sustainable fuels and chemicals for climate change solutions. In this field which merges electrochemistry with nanomaterials, there is an urgent need to discover new catalytic materials. One example of the paradigms shifting in this area concerns the production of nanoparticles of complex metal alloys ("high entropy alloys"), which offer billions of plausible composition and synthesis [1]. However the multiple chemical compositions offered requires not only theoretical chemistry approaches but also high throughput multi-correlative microscopy experimental characterizations to find the best electrocatalysts.

Ideally finding the best electrocatalytic nanoparticles requires evaluating their intrinsic activity, typically reached through a monitoring *in situ*, in real time and at the single nanoparticle level [2]. Our group proposes the use of optical microscopies, correlated to *ex situ* scanning electron microscopy, and local electrochemical probing, as a means to unravel complex electrochemical mechanisms (Figure). Despite the poor imaging resolution of optical microscopy compared to electron microscopies, quantitative optical strategies allow visualizing and quantifying various nanoscale processes while imaging nanoobjects with a detection limit below 20nm in size. Such detection limit, under operating conditions meaning in solution and during an electrochemical generation process, relies on the use of highly sensitive interference-based optical microscopies (see for example the promise of iSCAT [3]). Moreover, the interference contrast offered by such microscopies allows differentiation various phenomena such as phase transformation or products generation and differentiating nanoparticles of different composition (*e.g.* metals from metal oxides). They also provide access to high throughput benchmarking. Indeed the electrochemical behavior of thousands of individual nanoparticles can be analyzed over $<50x50\mu m^2$ regions imaged. Combined with micro- to nanopipettes probes one can confine micro to nanosized droplets of electrolyte on a macroscopic electrode and form micro- to nanoelectrochemical cells which can provide, from their individual imaging, a statistical evaluation of the heterogeneity of macroscale electrochemical behaviors.

This communication illustrates some of our recent results using these multi-microscopies approaches, from the micro to nanoscale. Two situations encountered in electrocatalysis will be explored concerning either the electrochemical deposition of electrocatalytic nanoparticles or their use to produce gas nanobubbles by electrocatalysis.

The first one (Figure a) consists in the preparation of electrocatalytic materials [4], here arrays of Ni-based nanoparticles, metal Ni or Ni-hydroxides, which are prepared by electrodeposition processes. It is particularly shown how both materials can be differentiated from their differing optical properties, and how this can be used to reveal new mechanistic insights in the dynamics of their nucleation/growth.

In a second example in Figure b [5], the electrogeneration of gaseous products, H_2, from the hydrogen evolution reaction at electrocatalytic Pt nanoparticles is detailed. Optical microscopy then allows a quantitative assessment of the dynamics of electrogeneration of individual H_2 nanobubbles, providing a

quantitative assessment of the dynamics of electrogeneration of individual H_2 nanobubbles, providing a pseudo-3D visualization of the nanobubble growth.

References:

[1] TAA Batchelor *et al*, Angew. Chemie Int. Ed. **60** (2021) p. 6932.
[2] LA Baker, J. Am. Chem. Soc. **140** (2018) p. 15549.
[3] RW Taylor and V Sandoghdar, Nano Lett. **19** (2019) p. 4827.
[4] L Godeffroy *et al*, Angew. Chemie - Int. Ed. **60** (2021) p. 16980.
[5] J-F Lemineur *et al*, ACS Nano **15** (2021) p. 2643.
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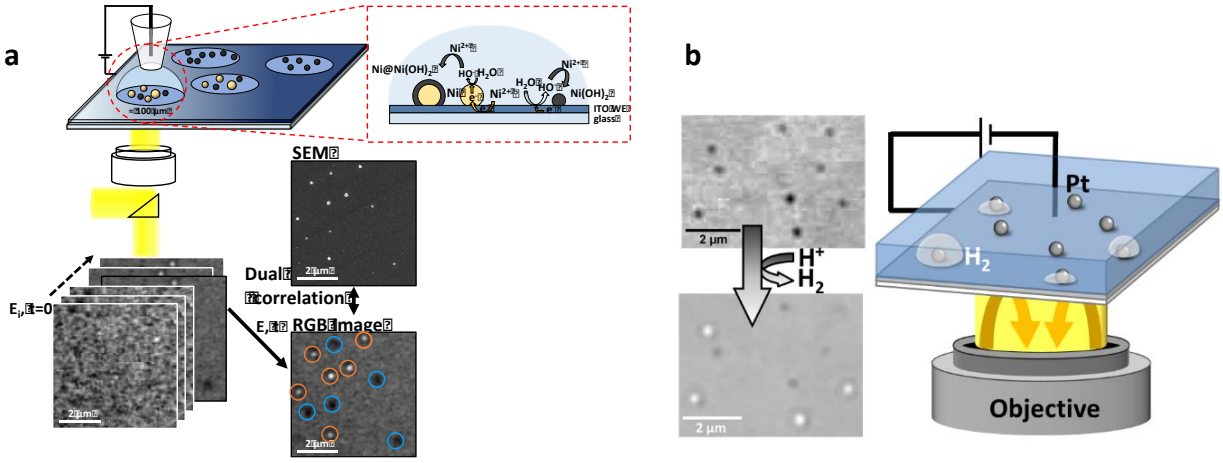

Figure 1. (a) Correlated SEM and optical microscopy imaging of the electrodeposition of Ni (orange circles or bright objects) and $Ni(OH)_2$ (blue circles and dark objects) nanoparticles. Adapted with permission from Reference [4]. Copyright 2021, John Wiley & Sons. (b) Monitoring the electrogeneration of H_2 nanobubbles electrogenerated at individual 40 nm Pt nanoparticles; Reprinted with permission from reference [5]. Copyright 2021, American Chemical Society.

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