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Watching operando nanoscale electrochemical deposition by optical microscopy

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Abstract

Electrodeposition is a popular electrochemical technique which has recently shifted from the deposition of conformal thin films to the deposition of nanoparticles and the fabrication of nanostructured electrodes. It is straightforward to implement for catalysis and sensing applications and it allows producing surfactant-free and perfectly connected nanoparticles whose size, shape and composition can be modulated by the applied potential or current. Meanwhile, the underlying mechanisms of nanoparticle nucleation and growth are still under intensive investigation thanks to the considerable technological improvements made in many high resolution (*operando* or identical location) imaging techniques over the last two decades. This review focuses on the recent advances made by optical microscopy in this field. It is indeed now possible to use high resolution optical microscopes to probe objects noninvasively and *operando* at the nanoscale with a very high temporal resolution and high throughput, which is of particular interest for electrodeposition studies.

Keywords: Optical microscopy, electrodeposition, nanoelectrochemistry, high resolution operando imaging, single nanoparticle.

Highlights:

- Optical microscopy to monitor electrodeposition processes at the nanoscale.
- High throughput, high spatial and temporal resolution operando imaging.
- Visualizing competing processes during single nanoparticle growth.
- Super-localization, counting and sizing at the single nanoparticle level
- Monitoring the electrodeposition onto single nanoparticles
- Synergistic coupling between optical microscopy and electrochemical nano-tools.

Introduction

Electrodeposition has been an extremely popular electrochemical technique for quite a long time now. Even if it was initially developed for obtaining conformal electrode material coatings, which is still actively investigated with multi-component coatings [1], it has recently shown promise for synthesizing highly electro-active nanoparticles (NPs) with precise composition [2] and perfect connection with the electrode surface [3]. As the electrodeposit growth kinetics are driven by the applied potential or current, the size, shape and surface density of the resulting NPs can be finely controlled, which allows their integration in operational devices for sensing, energy or catalytic applications, to name but a few [4–6].

Analyzing the current traces recorded during electrodeposition gives valuable information on the nucleation mechanism and growth mode of the electrodeposit [7–9]. However, in numerous examples, they also fail to describe the number of growth or NP sites. It certainly explains why electrodeposition has been inspected extensively by a broad range of complementary *in situ*, identical location imaging or *operando* techniques [10]. For NP electrodeposition, high resolution imaging tools are required such as scanning probe microscopy (SPM) [11], transmission electron microscopy (TEM) [12–14], scanning electron microscopy (SEM) [15], etc. The collected data notably evidenced that NPs are formed by the surface aggregation of ultra-small nuclei [6,14,16,17].

Optical microscopies have been proposed a long time ago as a means to depict *in situ* the growth of objects during electro-crystallization [18,19]. These methods were mostly constrained to counting low population densities of objects $> 10 \mu\text{m}$ in size, so as not to cope with the resolution and detection limits of optical systems. The last two decades have witnessed tremendous technical and fundamental advances in optics, such as the development of highly sensitive, resolved and rapid digital cameras, or of the field of nano-optics and super-resolution concepts. Modern optical microscopies now allow the detection of objects whose size, density or characteristic formation time is improved by several orders of magnitude (about 3). Compared to the imaging techniques mentioned above, optical microscopy often enables faster acquisition rates and higher throughput without disturbing the NPs or their diffusion layer. However, care must be taken to the illumination conditions and high light power irradiation should be avoided as it may occasionally induce solution heating, convection or even trigger photochemical reaction which may distort the visualization. Optical microscopy also allows versatility in the experimental configurations, as individual NPs can be probed on macro-scale electrodes, within micro- and nano-scale droplet cells, or at the tip-end of a nano-electrode (see Figure 1 and indexes i, ii, and iii, respectively). All this makes a significant improvement to the *operando* monitoring of electrochemical processes [20–23], and particularly for electrodeposition studies, which are reviewed herein.

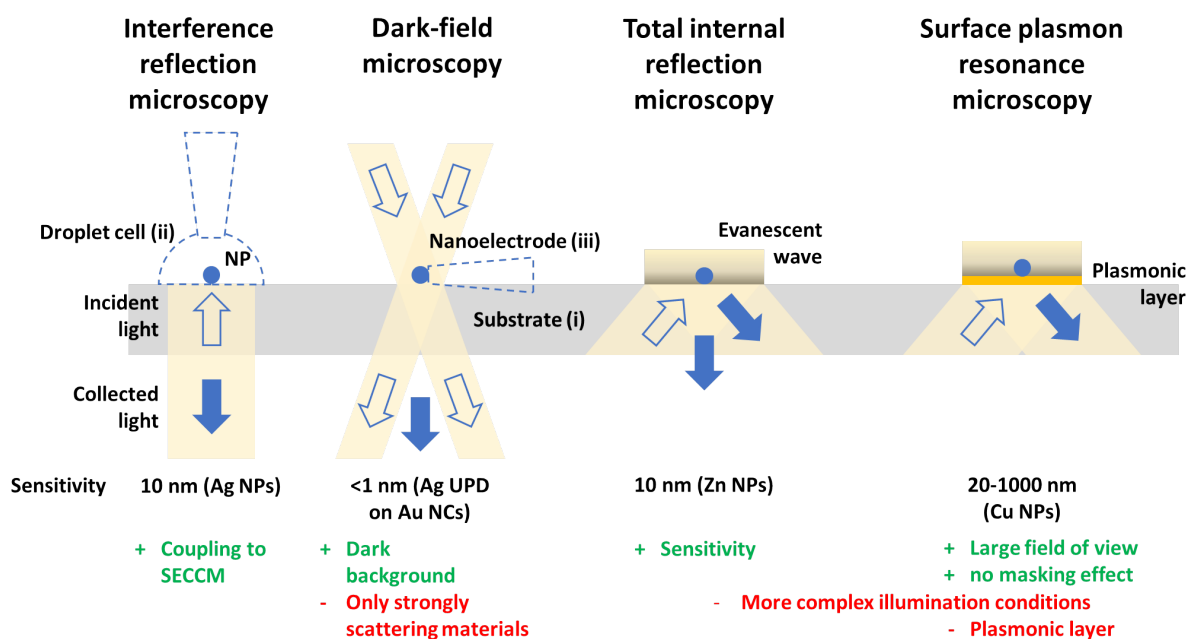


Figure 1. Most represented experimental configurations when coupling optical microscopy and electrochemistry. Individual NPs can be probed at a macro-scale electrode (i), within micro- or nano-scale droplet cell (ii) and at the tip-end of a nanoscale electrode (iii). Figure adapted from Ref. [20] (CC BY 4.0).

Monitoring the electrodeposition of nanostructures at macroscopic electrodes.

Sizing, counting individual NPs and assigning their growth dynamics

Pan *et al.* were the first to use high resolution optical microscopy (in this case dark-field microscopy, DFM) to directly observe the electrodeposition of individual NPs [24]. In DFM, the scattering intensity of a NP, which can be extracted from its optical image, is found to be linked to its size, in agreement with the Mie theory. A calibration, which can be achieved by correlating optical and SEM images, is important to ensure that optical microscopy provides a quantitative read-out of NP size or volume. By differentiating the dynamic NP volume change during the electrodeposition process, one can then reconstruct voltametric curves corresponding to the growth of single NPs, which are inaccessible to traditional electrochemical techniques. These curves revealed for instance heterogeneities in redox potential among Ag NPs. Two years later, combining DFM and fluorescence microscopy (FM), they showed that the redox potential distribution was dependent on the nature of the electrolyte [25]. DFM and FM provided similar information during the formation of the Ag NPs but proved to be complementary during their oxidation as DFM allows the detection of smaller NPs, while photoluminescence is much more sensitive to the formation of an oxide shell around the NPs.

Since these pioneering works, many studies were devoted to understanding the oxidation of Ag NPs using various optical methods [26–29]. These studies are out of the scope of this review but the work by Willets *et al.* is still worth mentioning as it shows that at high anodic potentials, the Ag^+ ions produced by the electrodisolution of Ag NPs electrodeposit as Ag-oxide NPs at a spatially distinct site [30].

Instead of acquiring the scattering of nano-objects by DFM in a trans-illumination mode, collection in a reflection mode often provides higher sensitivity. Different reflectance-based microscopies have been used to inspect electrodeposition mechanisms, such as surface plasmon resonance microscopy (SPRM) operated under oblique incidence or several interference reflection microscopies (IRM, e.g. the popular interferometric scattering microscope, iScatt [31]). Their enhanced sensitivity enables the detection of smaller NPs and therefore at their earlier electrodeposition stages. Recently, the electrodeposition of Ag NPs was revisited extensively by such IRM technique [32–34]. Correlating optical and SEM images allowed reconstructing cyclic voltammograms (CVs, Figure 2a) associated to single Ag NPs down to 10 nm in size. Finally, the authors highlight the advantage of electrodeposition as a methodology to produce platforms of surface-immobilized NPs with a wide range of sizes, which can be further used to investigate size effects in oxidation and reduction processes. The electrodeposition of Cu NPs was similarly studied by Mirsky *et al.* using wide-field (WF)-SPRM [35]. In this configuration, the optical signal was found to be proportional to the radius of the NP (in agreement with theoretical optical calculations). It means that small objects (20 nm) can be detected along much larger ones (>1000 nm) without any masking effect.

A further interest of the optical monitoring is its ability to measure *in situ* the growth rate of individual NPs, even in 3D using holographic microscope [36]. By analyzing the derivative of an image sequence taken during NP electrodeposition, one can discriminate between a growth controlled by charge transfer or reactant diffusion. A gradual change from these two growth regimes with increasing over-potential and reaction time could be observed for the electrodeposition of Cu NPs.

At higher NP surface density, the growth regime is governed by the overlapping of the diffusion layers as depicted in Figure 2b. This situation, theoretically addressed by different models, was confirmed by a quantitative reconstruction of the diffusion layers of all individual NPs [34] in a region of interest (ROI). This regime also explains that NPs which nucleate later are likely to do so within the diffusion layer of an existing one, resulting in a slower growth [34,35]. The crosstalk between NPs was also highlighted through an electrochemical Ostwald ripening between neighboring Ag NPs [32].

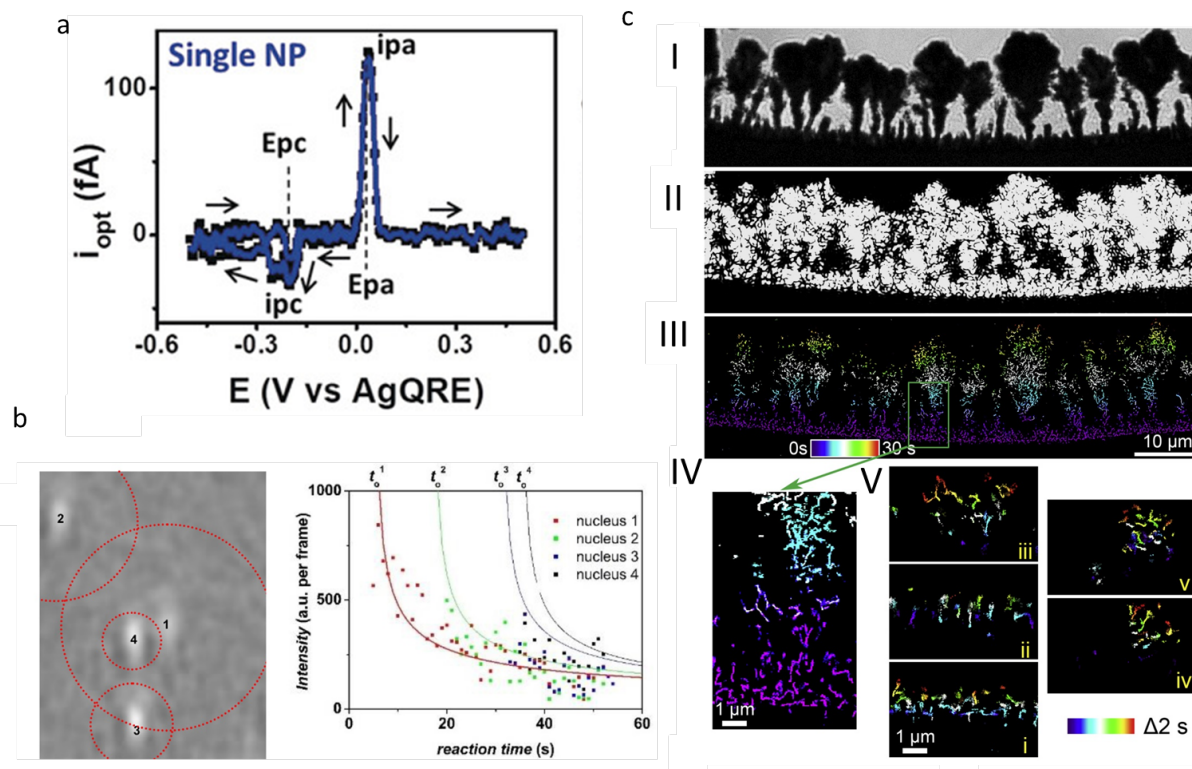


Figure 2. (a) Optical CV associated to an individual Ag NP built by differentiating the local optical intensity and made quantitative by correlation with SEM [32]. Copyright 2018 John Wiley & Sons. (b) Fragment of SPRM image of four distinct nuclei as well as their calculated diffusion zones and kinetics. The growth rate of NP 4 is directly controlled by the diffusion zone of NP 1 [35]. Copyright 2021 Elsevier. (c) Imaging (bright-field, I, dark-field, II, temporal color-coded super resolution, III, images) of Zn dendrite growth in ZnSO₄. IV is a zoom of III and V is a series of temporal images showing the early-stage growth of the dendrites [37]. Copyright 2021 Elsevier.

Introducing chemical complexity: competing reactions and super-resolution imaging.

It is only recently that the field of single-NP optical imaging moved beyond model noble metals. Optical microscopies were recently used to monitor the electrodeposition of metals presenting electro-catalytic properties such as Ni, Co, or used as batteries electrodes such as Li or Zn, or to monitor the electro-crystallization of metal oxides for energy storage/conversion applications (Co-oxides, Ni(OH)₂, MnO₂) or CO₂ capture (CaCO₃).

The reduction of Ni²⁺ ions in aqueous solution yields metallic Ni NPs, but also Ni(OH)₂ NPs owing to the ability of Ni to electro-catalyze either the reduction of O₂ or water [38]. The formation of each type of NP depends on the experimental conditions and the surface state of the electrode. Correlative multi-microscopy approaches, for example combining optical microscopy with AFM or SEM, are essential to identify the structure of the electrodeposited NPs [39]. From same-location optical and SEM imaging, it is shown that each type of NP can be differentiated optically. However, such strategy is often time-consuming. Recent artificial intelligence strategies, such as machine-vision ones, make the task easier. The automatized analysis of images acquired from different microscopies enables the recognition of specific patterns of NP deposits (template matching). It ensues the identification and clustering of

the chemical structure and dimensions of individual NPs [20,40], allowing for example to access the electro-catalytic activity of Ni NPs towards water reduction.

Monitoring electrodeposition processes under high current density is crucial for understanding the charge/discharge of battery electrodes. The charge of metal anodes, such as Li [41,42], Zn [37] or Mg [43], has been monitored by optical microscopies with different spatial resolutions. They were able to probe the nucleation and growth of metal dendrites, even in 3D by stimulated Raman spectroscopy imaging [42], which impede their practical applications in batteries. Although Zn is a poorly scattering metal compared to Ag, Au or Cu, a super-resolution strategy could be proposed [37] to (i) resolve single Zn nuclei with a 10 nm resolution and (ii) reconstruct the “real” image of the Zn dendrites at the nanoscale (Figure 2c). The role of current density and zinc salt concentration on Zn nucleation and growth was clearly evidenced at the single-nucleus level. In particular, it was demonstrated that at low concentrations, zinc depletion favors side reactions and electrode passivation, leading to higher current densities in the unblocked regions and hence to a highly directional growth which should be avoided.

Monitoring electrodeposition at miniaturized electrodes

Over the years, optical microscopies (especially DFM and FM) have also been used to inspect electrochemical processes within nano-electrochemical cells. These cells are defined by a miniaturized nano-electrode (Figure 1, index iii), or by the confinement of an electrochemical process inside a nano-pore, a nano-fluidic channel, a nano-metric cavity obtained by lithography, or defined by a meniscus cell confined between a micro- or nano-pipet filled with an electrolyte and a substrate (i.e. Scanning electrochemical cell microscopy or SECCM, Figure 1, index ii). The goal of such nano-confinement is to trap individual objects or molecules in order to study them and reach their intrinsic activity. With respect to electrodeposition, they allow to probe the nucleation/growth of a single NP and its further electrochemical analysis. DFM has been used to monitor the electrodeposition of a single NP at the tip-end of a nano-electrode to be used as platforms for EC-SERS [44], electro-catalysis [45–47] or sensing [48]. Pan *et al.* used DFM to size Au NPs electrodeposited at the apex of a sharp (30 nm) W tip [45]. Even when the NPs were smaller than the diffraction limit and could therefore not be properly sized, DFM was still able to detect *in situ* if a NP grew at the apex or not as the success rate of this process is very low.

Brasiliense *et al.* used the same approach for Au NPs electrodeposited on carbon nano-electrodes and obtained a good agreement between DFM and SEM [44]. The glass nanopipettes used to prepare the nanoelectrodes have the advantage of being perfectly insulated so unlike for the W tips, a correlation between final size and maximum current could be drawn. By comparing the evolution of the maximum current with the final size to that of the expected steady-state current at a spherical electrode, a roughness factor could be estimated, confirming the fractal shape of the NPs observed by SEM.

Even if the actual size of the NP cannot be determined by DFM because of the diffraction limit, size variations down to 10-20 nm can still be measured using edge super-localization techniques. This approach was used to study the electrodeposition of individual Co-oxide

NPs on carbon nanoelectrodes [46,47] and their volumetric expansion during oxygen evolution [46]. It was shown that the optically derived CVs were more well-defined than the electrochemical CVs because they are only sensitive to the Co(II)/Co(III) transformation (electrochromism) and not to OER. The reversibility is also much less visible on the electrochemical CV, probably because Co(III) is involved in catalytic reactions. This complementary information, not accessible by single-NP electrochemistry alone, can then be used to study catalytic mechanisms.

The electrodeposition of single Ag, Au and Cu NPs on single nanopores within a self-assembled biomimetic membrane was also monitored by DFM [48]. Combined with FM of the labeled nanopores themselves, DFM demonstrated that the NPs selectively deposited in the center of the nanopores. Moreover, the growth of the NPs was followed via the plasmon resonance Rayleigh scattering peak shift, which can then be used to probe recognition binding events.

Finally, the experimental configuration of reflection-based microscopy enables the dynamic visualization of the approach and landing of a meniscus droplet cell onto a transparent substrate electrode (Figure 1, index ii). It further enables monitoring electrodeposition or electro-crystallization processes within such electrolyte droplet, providing complementary *operando* analysis of the electrochemistry going on in the scanning electrochemical cell configuration. It was used to follow the electrodeposition of Ni NPs [38,39] in micrometric droplets and the electro-crystallization of dielectric NPs, namely CaCO₃ NPs, upon oxygen reduction (ORR) on the electrode [49]. The number and spatial distribution of the crystals were shown to depend on applied potential and pipet size (down to 0.5 μm meniscus cell), hinting at a dynamic interplay between pipet mass transport, ORR rates at the ITO electrode, and CO₂/O₂ transport at the air/meniscus interface.

Monitoring electrodeposition at single NPs

As sketched in Figure 3, optical microscopy has also been used to monitor the electrodeposition of foreign material onto a NP used as template. It is beneficial to unravel these mechanisms (by identifying intermediates), and to design heterogeneous nanostructures of controlled (and more complex) morphologies. *In situ* optical investigations were mostly performed at plasmonic (Ag or Au) NPs, due to the high sensitivity of their localized surface plasmon resonance, LSPR, to many parameters such as their size, structure, facets, composition or surrounding environment [50].

The deposition of metal onto a plasmonic NP induces a shift in the LSPR spectrum by hundreds of nanometers which can then be detected optically as a change in color of the NP. This strategy was originally used to track the electrochemical amalgamation of Au nanorods by Hg upon reduction of Hg²⁺ ions [51,52]. In addition to monitoring the diffusion controlled deposition of Hg⁰, the optical data highlighted the slow insertion of mercury atoms within the nanorods, the concomitant shape transition from rod to sphere and volume expansion. Later, DFM showed that the NP restructuring could be avoided when the Au NPs were coated with a rigid but permeable to Hg²⁺ mesoporous SiO₂ shell [53].

Following on these works, Xu *et al.* probed by DFM the electrodeposition of mono and bi-metallic shells (Pt, Pd, Rh, PtPd and PdRh) onto template Au NPs [54]. Beyond the objective of producing novel photo-catalysts for the methanol oxidation reaction, the DFM imaging revealed two distinct deposition regimes (surface vs bulk). Initially, the nucleation of small metal clusters at the Au NP surface is detected as a NP color change without affecting the scattering intensity. Later, the increase of the scattering intensity rapidly reveals the thickening of the shell (bulk).

The high sensitivity of LSPR to NP surface alteration was pushed to the limit of *operando* imaging of the electrodeposition of Ag on Au NP with sub-atomic layer deposition detection [55]. The fine tuning of the deposition with atomic precision is afforded by under potential deposition (UPD). The process is monitored from color (LSPR wavelength) variations, and therefore by spectroscopic microscopy. This optical variation allows to build a CV at the single NP level, as illustrated in Figure 3a, impossible to reach from the electrochemical signature. Applied to truncated octahedral Au NPs, the optical CV discriminates and quantifies the UPD occurring on the two distinct facets exposed (peaks labeled as 1 and 2 in Figure 3a) and bulk deposition.

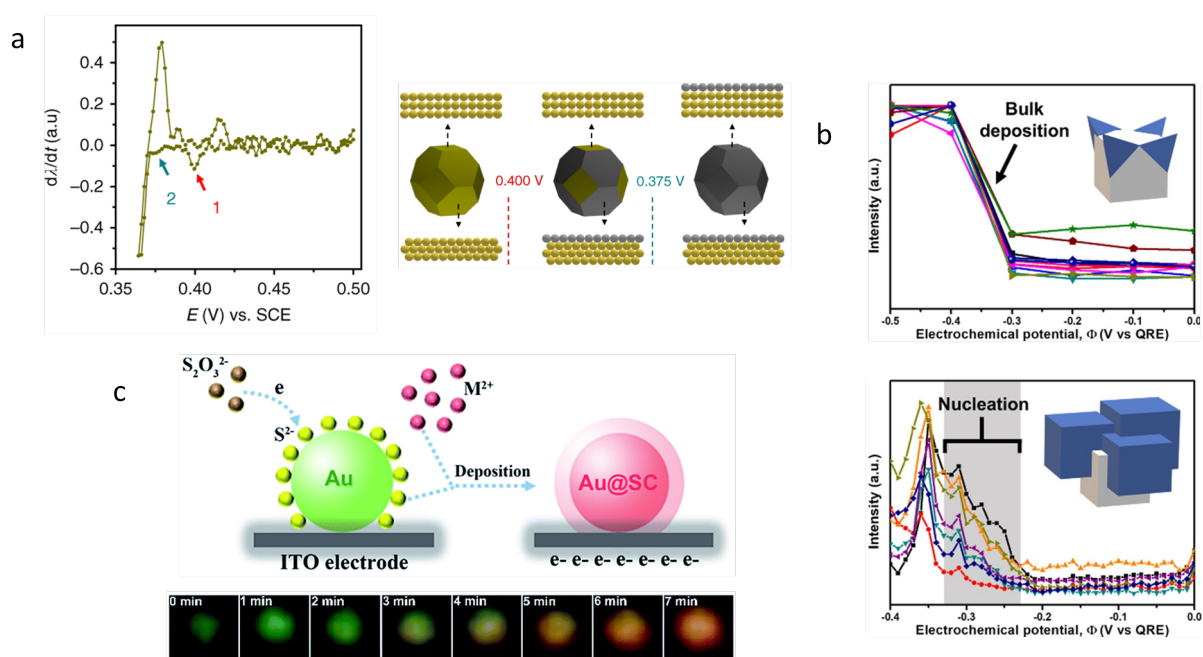


Figure 3. Monitoring electrodeposition of foreign material onto single NPs used as template. (a) Optical CV obtained from the differentiation of the LSPR wavelength fluctuation during the sub-atomic UPD of Ag on truncated octahedral Au NPs exposing two distinct facets [55]. (CC BY 4.0) (b) Optical monitoring of Cu deposition on Ag nanocubes by LSV that allows to discriminate morphology changes due to either bulk deposition or surface nucleation [56]. Copyright 2020 American Chemical Society. (c) Electrochemical deposition of a semiconducting shell on Au NPs probed and optimized by DFM [57]. (CC BY-NC 3.0)

The UPD of Cu on Ag nanocubes under linear sweep voltammetry (LSV) was monitored by DFM with similar sensitivity [56]. Moreover, by adjusting the potential scan rate, one could probe significant changes in the NP's morphology. As depicted in Figure 3b, if homogeneous bulk deposition is observed at high rates, slower rates favor multiple nucleation events and

selective growth on more reactive nanoscale edges and vertices. It also highlights the role of the capping agent present at the Ag cube surface on UPD.

Indeed, even if electrodeposition does not require any capping agent, its presence can greatly increase the complexity of the growth mechanism, mostly by modulating the electron transfer kinetics. The hindering effect of cysteine on Cu UPD kinetics was investigated at the single Ag nanocube level by optical microscopy [58]. Coupled to *ex-situ* SEM and optical simulations, the color and optical intensity variations allowed identifying the different intermediate morphologies (rough cube, cube-on-cube, octapod) formed during Cu deposition, up to that of the final complex (windmill-like morphology).

Interestingly, the strategy was extended to the electro-crystallization of semiconducting nanocrystal shells atop Au NPs as depicted in Figure 3c. Wang *et al.* [57] probed the electrochemical deposition of a CdS semiconducting shell at single Au NPs upon reduction of thiosulfate in the presence of Cd²⁺ cations. In acidic conditions and at sufficiently high cathodic potential, S₂O₃²⁻ is reduced into S²⁻ ions that adsorbed onto the NPs and triggered the precipitation of Cd²⁺ cations. With the help of *ex situ* SEM and optical simulations, the deposition dynamics was monitored optically from the gradual color change of the NPs. The method was then generalized to the deposition of ZnS and CdSe shells at Au NPs.

Conclusion

Electrodeposition is a fascinating and active field of research. It has been fueled within the last two decades by the constant developments of high resolution imaging instruments. This new generation of microscopes have enabled new mechanistic questions to be investigated, such as the observation and decoupling between surface nucleation and bulk (growth) processes.

Even if optical microscopy cannot reach the high spatial resolution of AFM/STM or TEM, it provides a simple and cost-effective solution for inspecting and quantifying electrodeposition processes *in situ* and in real time (*operando*). Optical microscopes provide high throughput (up to 10⁸ NPs per cm²), high spatial resolution and fast (up to kHz) imaging, and can straightforwardly be coupled to electrochemistry. NPs as small as 10 nm have been imaged dynamically, while their motion can be probed with sub-5 nm spatial resolution. The growth of a NP can then be monitored with sub-monolayer sensitivity, enabling to shift towards the understanding of electrodeposition mechanisms at or over a single NP and to discover new synthetic routes (new morphologies). From a mechanistic point of view, different types of nano-objects can be differentiated within a single experiment (using multi-color channel observation and/or multi-microscopy approaches complemented by machine learning), allowing to shed light on competing chemical processes.

Beyond the recent fundamental advances, it has also brought new strategies to apprehend more applied situations, in particular in the field of batteries. It requires looking not only through transparent electrodes, but also at highly reflective substrate electrodes, which can be achieved using water immersion objectives [59–61]. Optical microscopy already allowed to investigate the electro-crystallization and electro-dissolution of MnO₂ films during the

charge and discharge of aqueous Zn-MnO₂ batteries [60], and the formation of nanostructures (such as dendrites) at metal anodes under high current densities [37,41].

Finally, we anticipate that optical microscopy will be increasingly integrated into correlative microscopy strategies [39], allowing to collect highly complementary data that will further be manipulated and analyzed by machine learning algorithms [62].

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References

- [1] F.C. Walsh, S. Wang, N. Zhou, The electrodeposition of composite coatings: Diversity, applications and challenges, *Curr. Opin. Electrochem.* 20 (2020) 8–19. <https://doi.org/10.1016/j.coelec.2020.01.011>.
- [2] M.W. Glasscott, A.D. Pendergast, S. Goines, A.R. Bishop, A.T. Hoang, C. Renault, J.E. Dick, Electrosynthesis of high-entropy metallic glass nanoparticles for designer, multi-functional electrocatalysis, *Nat. Commun.* 10 (2019) 2650. <https://doi.org/10.1038/s41467-019-10303-z>.
- [3] W. Wei, T. Yuan, W. Jiang, J. Gao, H.-Y. Chen, W. Wang, Accessing the Electrochemical Activity of Single Nanoparticles by Eliminating the Heterogeneous Electrical Contacts, *J. Am. Chem. Soc.* 142 (2020) 14307–14313. <https://doi.org/10.1021/jacs.0c06171>.
- [4] M.B. Kale, R.A. Borse, A. Goma Abdelkader Mohamed, Y. Wang, Electrocatalysts by Electrodeposition: Recent Advances, Synthesis Methods, and Applications in Energy Conversion, *Adv. Funct. Mater.* 31 (2021) 2101313. <https://doi.org/10.1002/adfm.202101313>.
- [5] S.A. Lee, J.W. Yang, S. Choi, H.W. Jang, Nanoscale electrodeposition: Dimension control and 3D conformality, *Exploration.* 1 (2021) 20210012. <https://doi.org/10.1002/EXP.20210012>.
- [6] J. Ustarroz, Current atomic-level understanding of electrochemical nucleation and growth on low-energy surfaces, *Curr. Opin. Electrochem.* 19 (2020) 144–152. <https://doi.org/10.1016/j.coelec.2019.12.001>.
- [7] B.R. Scharifker, J. Mostany, Three-dimensional nucleation with diffusion controlled growth, *J. Electroanal. Chem. Interfacial Electrochem.* 177 (1984) 13–23. [https://doi.org/10.1016/0022-0728\(84\)80207-7](https://doi.org/10.1016/0022-0728(84)80207-7).
- [8] B. Scharifker, G. Hills, Theoretical and experimental studies of multiple nucleation, *Electrochim. Acta.* 28 (1983) 879–889. <https://doi.org/https://doi.org/10.1016/0013->

4686(83)85163-9.

- [9] M.E. Hyde, R.G. Compton, A review of the analysis of multiple nucleation with diffusion controlled growth, *J. Electroanal. Chem.* 549 (2003) 1–12. [https://doi.org/10.1016/S0022-0728\(03\)00250-X](https://doi.org/10.1016/S0022-0728(03)00250-X).
- [10] Y. Yang, Y. Xiong, R. Zeng, X. Lu, M. Krumov, X. Huang, W. Xu, H. Wang, F.J. DiSalvo, J.D. Brock, D.A. Muller, H.D. Abruña, Operando Methods in Electrocatalysis, *ACS Catal.* 11 (2021) 1136–1178. <https://doi.org/10.1021/acscatal.0c04789>.
- [11] J. V Zoval, R.M. Stiger, P.R. Biernacki, R.M. Penner, Electrochemical Deposition of Silver Nanocrystallites on the Atomically Smooth Graphite Basal Plane, *J. Phys. Chem.* 100 (1996) 837–844. <https://doi.org/10.1021/jp952291h>.
- [12] Y. Yang, Y.-T. Shao, F.J. DiSalvo, D.A. Muller, H.D. Abruña, Metal Monolayers on Command: Underpotential Deposition at Nanocrystal Surfaces: A Quantitative Operando Electrochemical Transmission Electron Microscopy Study, *ACS Energy Lett.* 7 (2022) 1292–1297. <https://doi.org/10.1021/acsenerylett.2c00209>.
- [13] A. Radisic, P.M. Vereecken, J.B. Hannon, P.C. Searson, F.M. Ross, Quantifying Electrochemical Nucleation and Growth of Nanoscale Clusters Using Real-Time Kinetic Data, *Nano Lett.* 6 (2006) 238–242. <https://doi.org/10.1021/nl052175i>.
- [14] H.E.M. Hussein, R.J. Maurer, H. Amari, J.J.P. Peters, L. Meng, R. Beanland, M.E. Newton, J. V. Macpherson, Tracking Metal Electrodeposition Dynamics from Nucleation and Growth of a Single Atom to a Crystalline Nanoparticle, *ACS Nano.* 12 (2018) 7388–7396. <https://doi.org/10.1021/acsnano.8b04089>.
- [15] P. Grosse, A. Yoon, C. Rettenmaier, S.W. Chee, B.R. Cuenya, Growth Dynamics and Processes Governing the Stability of Electrodeposited Size-Controlled Cubic Cu Catalysts, *J. Phys. Chem. C.* 124 (2020) 26908–26915. <https://doi.org/10.1021/acs.jpcc.0c09105>.
- [16] J. Ustarroz, J.A. Hammons, T. Altantzis, A. Hubin, S. Bals, H. Terry, A Generalized Electrochemical Aggregative Growth Mechanism, *J. Am. Chem. Soc.* 135 (2013) 11550–11561. <https://doi.org/10.1021/ja402598k>.
- [17] R.L. Harniman, D. Plana, G.H. Carter, K.A. Bradley, M.J. Miles, D.J. Fermín, Real-time tracking of metal nucleation via local perturbation of hydration layers, *Nat. Commun.* 8 (2017) 971. <https://doi.org/10.1038/s41467-017-01087-1>.
- [18] M. Wang, W.J.P. van Enkevort, N. Ming, P. Bennema, Formation of a mesh-like electrodeposit induced by electroconvection, *Nature.* 367 (1994) 438–441. <https://doi.org/10.1038/367438a0>.
- [19] A. Milchev, B. Scharifker, G. Hills, A potentiostatic study of the electrochemical nucleation of silver on vitreous carbon, *J. Electroanal. Chem. Interfacial Electrochem.* 132 (1982) 277–289. [https://doi.org/10.1016/0022-0728\(82\)85025-0](https://doi.org/10.1016/0022-0728(82)85025-0).
- [20] S. Nizamov, S.D. Sazdovska, V.M. Mirsky, A review of optical methods for ultrasensitive detection and characterization of nanoparticles in liquid media with a focus on the wide field surface plasmon microscopy, *Anal. Chim. Acta.* 1204 (2022) 339633. <https://doi.org/https://doi.org/10.1016/j.aca.2022.339633>.

- [21] J.-F. Lemineur, H. Wang, W. Wang, F. Kanoufi, Emerging Optical Microscopy Techniques for Electrochemistry, *Annu. Rev. Anal. Chem.* 15 (2022) 57–82. <https://doi.org/10.1146/annurev-anchem-061020-015943>.
- [22] J.-M. Noël, J.-F. Lemineur, Optical microscopy to study single nanoparticles electrochemistry: From reaction to motion, *Curr. Opin. Electrochem.* 25 (2021) 100647. <https://doi.org/10.1016/j.coelec.2020.100647>.
- [23] F. Kanoufi, Electrochemistry and Optical Microscopy, in: *Encycl. Electrochem.*, Wiley, 2021: pp. 1–80. <https://doi.org/10.1002/9783527610426.bard030108>.
- [24] C.M. Hill, S. Pan, A Dark-Field Scattering Spectroelectrochemical Technique for Tracking the Electrodeposition of Single Silver Nanoparticles, *J. Am. Chem. Soc.* 135 (2013) 17250–17253. <https://doi.org/10.1021/ja4075387>.
- [25] C.M. Hill, R. Bennett, C. Zhou, S. Street, J. Zheng, S. Pan, Single Ag Nanoparticle Spectroelectrochemistry via Dark-Field Scattering and Fluorescence Microscopies, *J. Phys. Chem. C.* 119 (2015) 6760–6768. <https://doi.org/10.1021/jp511637a>.
- [26] Y. Fang, W. Wang, X. Wo, Y. Luo, S. Yin, Y. Wang, X. Shan, N. Tao, Plasmonic Imaging of Electrochemical Oxidation of Single Nanoparticles, *J. Am. Chem. Soc.* 136 (2014) 12584–12587. <https://doi.org/10.1021/ja507097y>.
- [27] V. Brasiliense, A.N. Patel, A. Martinez-Marrades, J. Shi, Y. Chen, C. Combellas, G. Tessier, F. Kanoufi, Correlated Electrochemical and Optical Detection Reveals the Chemical Reactivity of Individual Silver Nanoparticles, *J. Am. Chem. Soc.* 138 (2016) 3478–3483. <https://doi.org/10.1021/jacs.5b13217>.
- [28] R. Hao, Y. Fan, B. Zhang, Imaging Dynamic Collision and Oxidation of Single Silver Nanoparticles at the Electrode/Solution Interface, *J. Am. Chem. Soc.* 139 (2017) 12274–12282. <https://doi.org/10.1021/jacs.7b06431>.
- [29] K. Wonner, M. V. Evers, K. Tschulik, Simultaneous Opto- and Spectro-Electrochemistry: Reactions of Individual Nanoparticles Uncovered by Dark-Field Microscopy, *J. Am. Chem. Soc.* 140 (2018) 12658–12661. <https://doi.org/10.1021/jacs.8b02367>.
- [30] V. Sundaresan, J.W. Monaghan, K.A. Willets, Monitoring Simultaneous Electrochemical Reactions with Single Particle Imaging, *ChemElectroChem.* 5 (2018) 3052–3058. <https://doi.org/10.1002/celec.201800715>.
- [31] R.W. Taylor, V. Sandoghdar, Interferometric Scattering Microscopy: Seeing Single Nanoparticles and Molecules via Rayleigh Scattering, *Nano Lett.* 19 (2019) 4827–4835. <https://doi.org/10.1021/acs.nanolett.9b01822>.
- [32] J.-F. Lemineur, J.-M. Noël, D. Ausserré, C. Combellas, F. Kanoufi, Combining Electrodeposition and Optical Microscopy for Probing Size-Dependent Single-Nanoparticle Electrochemistry, *Angew. Chemie Int. Ed.* 57 (2018) 11998–12002. <https://doi.org/10.1002/anie.201807003>.
- [33] J.-F. Lemineur, J.-M. Noël, C. Combellas, D. Ausserré, F. Kanoufi, The promise of antireflective gold electrodes for optically monitoring the electro-deposition of single silver nanoparticles, *Faraday Discuss.* 210 (2018) 381–395.

<https://doi.org/10.1039/C8FD00037A>.

[34] J.-F. Lemineur, J.-M. Noël, C. Combellas, F. Kanoufi, Optical monitoring of the electrochemical nucleation and growth of silver nanoparticles on electrode: From single to ensemble nanoparticles inspection, *J. Electroanal. Chem.* 872 (2020) 114043. <https://doi.org/10.1016/j.jelechem.2020.114043>.

[35] V.K. Laurinavichyute, S. Nizamov, V.M. Mirsky, Real time tracking of the early stage of electrochemical nucleation, *Electrochim. Acta.* 382 (2021) 138278. <https://doi.org/10.1016/j.electacta.2021.138278>.

* Optical monitoring reveals that NPs communicates during electrodeposition by the overlapping of their diffusion layers.

[36] A.P. Abbott, M. Azam, K.S. Ryder, S. Saleem, In Situ Electrochemical Digital Holographic Microscopy; a Study of Metal Electrodeposition in Deep Eutectic Solvents, *Anal. Chem.* 85 (2013) 6653–6660. <https://doi.org/10.1021/ac400262c>.

[37] X. Ye, M. Saqib, J. Mao, G. Li, R. Hao, Spatiotemporally super-resolved dendrites nucleation and early-stage growth dynamics in Zinc-ion batteries, *Cell Reports Phys. Sci.* 2 (2021) 100420. <https://doi.org/10.1016/j.xcrp.2021.100420>.

** Super-resolution optical microscopy strategy to apprehend a more applied situation, i.e. the growth of dendrites in batteries.

[38] L. Godeffroy, P. Ciocci, A. Nsabimana, M. Miranda Vieira, J.-M. Noël, C. Combellas, J.-F. Lemineur, F. Kanoufi, Deciphering Competitive Routes for Nickel-Based Nanoparticle Electrodeposition by an Operando Optical Monitoring, *Angew. Chemie Int. Ed.* 60 (2021) 16980–16983. <https://doi.org/10.1002/anie.202106420>.

[39] L. Godeffroy, J.-F. Lemineur, V. Shkirskiy, M. Miranda Vieira, J.-M. Noël, F. Kanoufi, Bridging the Gap between Single Nanoparticle Imaging and Global Electrochemical Response by Correlative Microscopy Assisted By Machine Vision, *Small Methods.* n/a (2022) 2200659. <https://doi.org/10.1002/smt.202200659>.

** Optical imaging integrated into a correlative microscopy approach assisted by machine learning.

[40] S. Nizamov, V. Scherbahn, V.M. Mirsky, Detection and Quantification of Single Engineered Nanoparticles in Complex Samples Using Template Matching in Wide-Field Surface Plasmon Microscopy, *Anal. Chem.* 88 (2016) 10206–10214. <https://doi.org/10.1021/acs.analchem.6b02878>.

[41] P. Bai, J. Li, F.R. Brushett, M.Z. Bazant, Transition of lithium growth mechanisms in liquid electrolytes, *Energy Environ. Sci.* 9 (2016) 3221–3229. <https://doi.org/10.1039/C6EE01674J>.

[42] Q. Cheng, L. Wei, Z. Liu, N. Ni, Z. Sang, B. Zhu, W. Xu, M. Chen, Y. Miao, L.-Q. Chen, W. Min, Y. Yang, Operando and three-dimensional visualization of anion depletion and lithium growth by stimulated Raman scattering microscopy, *Nat. Commun.* 9 (2018) 2942. <https://doi.org/10.1038/s41467-018-05289-z>.

[43] J.H. Kwak, Y. Jeoun, S.H. Oh, S. Yu, J.-H. Lim, Y.-E. Sung, S.-H. Yu, H.-D. Lim, Operando

Visualization of Morphological Evolution in Mg Metal Anode: Insight into Dendrite Suppression for Stable Mg Metal Batteries, *ACS Energy Lett.* 7 (2022) 162–170. <https://doi.org/10.1021/acsenerylett.1c02486>.

- [44] V. Brasiliense, J.E. Park, Z. Chen, R.P. Van Duyne, G.C. Schatz, Nanopipette-based electrochemical SERS platforms: Using electrodeposition to produce versatile and adaptable plasmonic substrates, *J. Raman Spectrosc.* 52 (2021) 339–347. <https://doi.org/10.1002/jrs.5974>.
- [45] Y. Wusimanjiang, Y. Ma, M. Lee, S. Pan, Single gold nanoparticle electrode for electrogenerated chemiluminescence and dark field scattering spectroelectrochemistry, *Electrochim. Acta.* 269 (2018) 291–298. <https://doi.org/10.1016/j.electacta.2018.02.154>.
- [46] V. Brasiliense, J. Clausmeyer, P. Berto, G. Tessier, C. Combellas, W. Schuhmann, F. Kanoufi, Monitoring Cobalt-Oxide Single Particle Electrochemistry with Subdiffraction Accuracy, *Anal. Chem.* 90 (2018) 7341–7348. <https://doi.org/10.1021/acs.analchem.8b00649>.
- [47] V. Brasiliense, J. Clausmeyer, A.L. Dauphin, J.-M. Noël, P. Berto, G. Tessier, W. Schuhmann, F. Kanoufi, Opto-electrochemical In Situ Monitoring of the Cathodic Formation of Single Cobalt Nanoparticles, *Angew. Chemie Int. Ed.* 56 (2017) 10598–10601. <https://doi.org/10.1002/anie.201704394>.
- [48] L.-X. Qin, Y. Li, D.-W. Li, C. Jing, B.-Q. Chen, W. Ma, A. Heyman, O. Shoseyov, I. Willner, H. Tian, Y.-T. Long, Electrodeposition of Single-Metal Nanoparticles on Stable Protein 1 Membranes: Application of Plasmonic Sensing by Single Nanoparticles, *Angew. Chemie Int. Ed.* 51 (2012) 140–144. <https://doi.org/https://doi.org/10.1002/anie.201106482>.
- [49] D. Valavanis, P. Ciocci, G.N. Meloni, P. Morris, J.-F. Lemineur, I.J. McPherson, F. Kanoufi, P.R. Unwin, Hybrid scanning electrochemical cell microscopy-interference reflection microscopy (SECCM-IRM): tracking phase formation on surfaces in small volumes, *Faraday Discuss.* (2022). <https://doi.org/10.1039/D1FD00063B>.

* Operando optical investigation of electrocrystallisation under confinement.

- [50] B.S. Hoener, S.R. Kirchner, T.S. Heiderscheid, S.S.E. Collins, W.-S. Chang, S. Link, C.F. Landes, Plasmonic Sensing and Control of Single-Nanoparticle Electrochemistry, *Chem.* 4 (2018) 1560–1585. <https://doi.org/10.1016/j.chempr.2018.04.009>.
- [51] C. Schopf, A. Wahl, A. Martín, A. O’Riordan, D. Iacopino, Direct Observation of Mercury Amalgamation on Individual Gold Nanorods Using Spectroelectrochemistry, *J. Phys. Chem. C.* 120 (2016) 19295–19301. <https://doi.org/10.1021/acs.jpcc.6b04668>.
- [52] J.-G. Wang, J.S. Fossey, M. Li, T. Xie, Y.-T. Long, Real-Time Plasmonic Monitoring of Single Gold Amalgam Nanoalloy Electrochemical Formation and Stripping, *ACS Appl. Mater. Interfaces.* 8 (2016) 8305–8314. <https://doi.org/10.1021/acsami.6b01029>.
- [53] Y.Y. Alizar, J.W. Ha, Single-particle spectroelectrochemistry: electrochemical tuning of plasmonic properties via mercury amalgamation in mesoporous silica coated gold nanorods without structural deformation, *Analyst.* 147 (2022) 2035–2039.

<https://doi.org/10.1039/D2AN00559J>.

- [54] H. Wang, W. Zhao, Y. Zhao, C.-H. Xu, J.-J. Xu, H.-Y. Chen, Real-Time Tracking the Electrochemical Synthesis of Au@Metal Core–Shell Nanoparticles toward Photo Enhanced Methanol Oxidation, *Anal. Chem.* 92 (2020) 14006–14011. <https://doi.org/10.1021/acs.analchem.0c02913>.
- [55] S. Hu, J. Yi, Y.-J. Zhang, K.-Q. Lin, B.-J. Liu, L. Chen, C. Zhan, Z.-C. Lei, J.-J. Sun, C. Zong, J.-F. Li, B. Ren, Observing atomic layer electrodeposition on single nanocrystals surface by dark field spectroscopy, *Nat. Commun.* 11 (2020) 2518. <https://doi.org/10.1038/s41467-020-16405-3>.

** Pushing the detection limit by imaging sub-atomic layer deposition on multi-faceted NPs.

- [56] H. Oh, Y. Park, H. Song, Tracking Underpotential Deposition of Copper on Individual Silver Nanocubes by Real-Time Single-Particle Plasmon Scattering Imaging, *J. Phys. Chem. C.* 124 (2020) 20398–20409. <https://doi.org/10.1021/acs.jpcc.0c05258>.
- [57] H. Wang, W. Zhao, C.-H. Xu, H. Chen, J. Xu, Electrochemical synthesis of Au@semiconductor core–shell nanocrystals guided by single particle plasmonic imaging, *Chem. Sci.* 10 (2019) 9308–9314. <https://doi.org/10.1039/C9SC02804H>.

* Operando optical microscopy to help designing complex heterogeneous nanostructures.

- [58] H. Oh, H. Hwang, H. Song, Structural complexity induced by {110} blocking of cysteine in electrochemical copper deposition on silver nanocubes, *Nanoscale.* 13 (2021) 1777–1783. <https://doi.org/10.1039/D0NR07470E>.
- [59] S. Munteanu, J.P. Roger, Y. Fedala, F. Amiot, C. Combellas, G. Tessier, F. Kanoufi, Mapping fluxes of radicals from the combination of electrochemical activation and optical microscopy, *Faraday Discuss.* 164 (2013) 241. <https://doi.org/10.1039/c3fd00024a>.
- [60] L. Godeffroy, I. Aguilar, J. Médard, D. Larcher, J.-M. Tarascon, F. Kanoufi, Decoupling the Dynamics of Zinc Hydroxide Sulfate Precipitation/Dissolution in Aqueous Zn–MnO₂ Batteries by Operando Optical Microscopy: A Missing Piece of the Mechanistic Puzzle, *Adv. Energy Mater.* n/a (2022) 2200722. <https://doi.org/10.1002/aenm.202200722>.
- [61] J.-F. Lemineur, T.J. Stockmann, J. Médard, C. Smadja, C. Combellas, F. Kanoufi, Optical Nanoimpacts of Dielectric and Metallic Nanoparticles on Gold Surface by Reflectance Microscopy: Adsorption or Bouncing?, *J. Anal. Test.* 3 (2019) 175–188. <https://doi.org/10.1007/s41664-019-00099-8>.
- [62] P. Unwin, Concluding remarks: next generation nanoelectrochemistry – next generation nanoelectrochemists, *Faraday Discuss.* (2022). <https://doi.org/10.1039/D2FD00020B>.