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Mini review

In situ and *operando* characterization techniques for nanocatalyst-based electrochemical hydrogen evolution reactions

Anaclet Nsabimana[1], Yiran Guan[2,✉], Guobao Xu[2,3,✉]

[1]*Chemistry Department, College of Science and Technology, University of Rwanda, P.O. Box: 3900, Kigali, Rwanda*
[2]*State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Jilin 130022, China*
[3]*School of Chemistry and Applied Engineering, University of Science and Technology of China, Hefei, Anhui 230026, China*

Corresponding authors: ✉guanyr@ciac.ac.cn; ✉guobaoxu@ciac.ac.cn; Tel.: +86-431-85262747; Fax: +86-431-85262747

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Abstract

The hydrogen evolution reaction is important in energy conversion and storage. This has led to the design of different types of catalysts and production setups. Understanding the status of the catalysts and reaction mechanisms motivated researchers to adopt the operando/in situ *techniques. Herein, we present a brief overview of the recent (from 2020) advances in the use of* in situ *and* operando *characterization techniques, such as* in situ *X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction analysis, IR spectroscopy, electrochemical Raman spectroscopy, online inductively coupled plasma - mass spectroscopy, differential electrochemical mass spectroscopy, optical microscopy, electron microscopy, electrochemical atomic microscopy, electrochemical scanning tunneling microscopy, and scanning electrochemical microscopy, in the electrochemical hydrogen evolution reaction. Representative examples of the applications of these techniques are also provided. Challenges in this field and future perspectives are discussed.*

Keywords

Electrocatalyst; *operando* technique; *in situ* characterization techniques; hydrogen evolution reaction

Introduction

The growth of the population and standards of living style increase the consumption of energy. Moreover, the use of fossil fuels is linked to environmental pollution and global warming. This motivated researchers to find sustainable and green energy. Hydrogen is one of the most promising sustainable and clean energy carriers, and it yields only water as a byproduct without any polluting emissions [1]. It is considered a potential fuel as it can be used as fuel free from carbon emissions, as an energy carrier, a storage medium, and in fuel cells [2]. Hydrogen is the best option for sustainable and secure energy because of its high energy density of 142.351 MJ kg^{-1} and its zero-emission profile [3].

Hydrogen produced using electrocatalytic water splitting has attracted ever-growing attention compared to the traditional method through steam from fossil fuels [4]. Hydrogen is obtained through the hydrogen evolution reaction (HER). The HER is the cathodic water electrolysis reaction, which can be performed in an acidic or alkaline medium [5]. In an alkaline solution, the HER reaction pathway is similar to that in an acidic environment but two to three orders of magnitude slower than that in an acidic medium [6]. For the synthesis of highly efficient HER electrocatalysts, several key characteristics, such as Gibbs free energy, minimum overpotentials in electrochemical HER, reduced Tafel slop, and enhanced exchange current density in electro-catalytical water splitting, *etc*, are sought [7].

Electrocatalysis has been fundamental in improving energy efficiency, reducing environmental impacts and carbon emissions, and promoting a more sustainable approach to meeting global energy demands [8]. However, its production efficiency through electrolysis of water is very low to be economically competitive because of the high energy consumption and low hydrogen evolution rate [1]. For this reason, more research has been conducted to increase efficiency and reduce energy consumption to develop alternative low-cost electrocatalysts with high efficiency. Nanomaterials with various chemical and physical structures are among the most promising electrocatalysts for HER. They are utilized for electrocatalysis due to their attractive properties, including high surface area, high catalytic activity and favourable nanoscale effects [8].

HER is a pivotal process in renewable energy conversion and storage systems, including electrolyzers, which transform and store intermittent renewable electricity into chemical energy by generating hydrogen [9]. However, it interferes with other energy production and conversion processes, such as N_2- and CO_2-reducing electrolyzers, batteries and, supercapacitors. Thus, understanding the structure and reaction mechanisms of electrocatalysts at electrode-electrolyte interfaces is crucial for the advancement of renewable energy technologies [8]. It is very important to understand the hydrogen adsorption and absorption mechanisms on the electrode surface because, for a constant HER rate at the electrode surface, the required overpotential decreases when the energetics of adsorption of reaction intermediates on the electrode surface is favorable [10]. Also, the electrocatalytic reactions are highly influenced by the morphology and surface composition of nanosized catalysts, with the electronic structure and atomic arrangement often determining their electrocatalytic performance [8]. Even though traditional characterization techniques provide some information, they are not suitable for real-time study of the nanocatalysts used in HER [11]. The *ex situ* characterization comparison between the pre- and post-chemical states of the catalyst in specific electrochemical reactions cannot always guarantee a meaningful trend and relevance between the chemical variation of the catalyst and electrochemical activity [12]. Thus, the need to address the working structure of a catalyst under reaction or working conditions has given rise to the development of *in situ* and *operando* methods [13,14]. To achieve that, the specialized reaction cells were integrated into conventional characterization instruments to facilitate the study of catalytic materials during the reactions, enabling the combination of data from conventional characterization of a sample under reaction conditions with simultaneous measurements of its catalytic performance.

This study provides a brief overview of recent advances in the application of the *in situ* and *operando* characterization techniques, such as *in situ* X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction (XRD) analysis, IR spectroscopy, electrochemical Raman spectroscopy, online inductively coupled plasma - mass spectroscopy, differential electrochemical mass spectroscopy, optical microscopy, electron microscopy, electrochemical atomic microscopy, electrochemical scanning tunneling microscopy, and scanning electrochemical microscopy, in the electrochemical hydrogen evolution reaction. Examples are also provided for each characterization technique.

In situ **and** ***operando*** **characterization techniques for electrochemical hydrogen evolution reactions**

X-ray adsorption spectroscopy

The energy of the X-rays is high enough to excite core-level electrons to higher unoccupied states. X-ray absorption spectroscopy (XAS) is one technique for measuring changes in X-ray absorption or fluorescence [8]. XAS is a technique that gathers data on the interactions between incoming X-rays and the core electrons within atoms [15]. XAS spectra can be categorized into three distinct regions, which are the pre-edge region, X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) [8,15]. XANES provides element-specific insights into the electronic structure, bonding geometry of the absorbing atom, and the density of unoccupied states [15]. In general, the spectrum of this region is located between the edge and 50 eV above the threshold [16]. On the other hand, EXAFS offers insights into local structures, including bond distances and coordination numbers around the absorbing atoms [15]. *In situ/operando* XAS is utilized to identify the electronic and geometric structures of electrocatalysts within electrode networks, particularly to elucidate the structure of active catalytic sites on oxide-based catalysts [16]. It provides detailed information about their electronic structures, coordination environments, and site symmetry, which are particularly effective in distinguishing different elements within multimetallic metal oxides [8].

Ding *at al.* [17] utilized XAS and near-ambient pressure X-ray photoelectron spectroscopy to reveal that NiS undergoes an *in-situ* phase transition to a mixed phase of Ni_3S_2 and NiO, creating highly active synergistic dual sites at the Ni_3S_2/NiO interface (Figure 1). The results showed that the interfacial Ni is the active site for water dissociation and OH* adsorption, while the interfacial S is the active site for H* adsorption and H_2 evolution [17]. Consequently, the in-situ formation of Ni_3S_2/NiO interfaces allowed NiS electrocatalysts to achieve an overpotential of only 95 ± 8 mV at a current density of 10 mA cm^{-2}.

Using *operando* EXAFS and XANES, Tang *et al.* [18] studied the Pt single-site catalysts and demonstrated that when a negatively biased potential is applied, the Pt−N bonds break first and then the Pt−Cl bonds follow. Pt is reduced from platinum(II) to metallic platinum(0) by the onset of the hydrogen-evolution reaction at 0 V. Furthermore, there was an increase in Pt−Pt bonding, which indicates the formation of Pt agglomerates.

Wang *et al.* [19] utilized Pt single atoms anchoring on the nitrogen-carbon substrate (PtSA/N-C) to investigate the dynamic structure of Pt single-atom centers during the HER process using *in situ/operando* synchrotron X-ray absorption spectroscopy and X-ray photoelectron spectroscopy. This helped to identify the intriguing structural reconstruction at the atomic level in the PtSA/N-C when it underwent repetitive cyclic voltammetry and linear sweep voltammetry scanning. It was demonstrated that the Pt-N bonding tends to be weakened under cathodic potentials, inducing some Pt single atoms to dynamically aggregate to form small clusters during the HER.

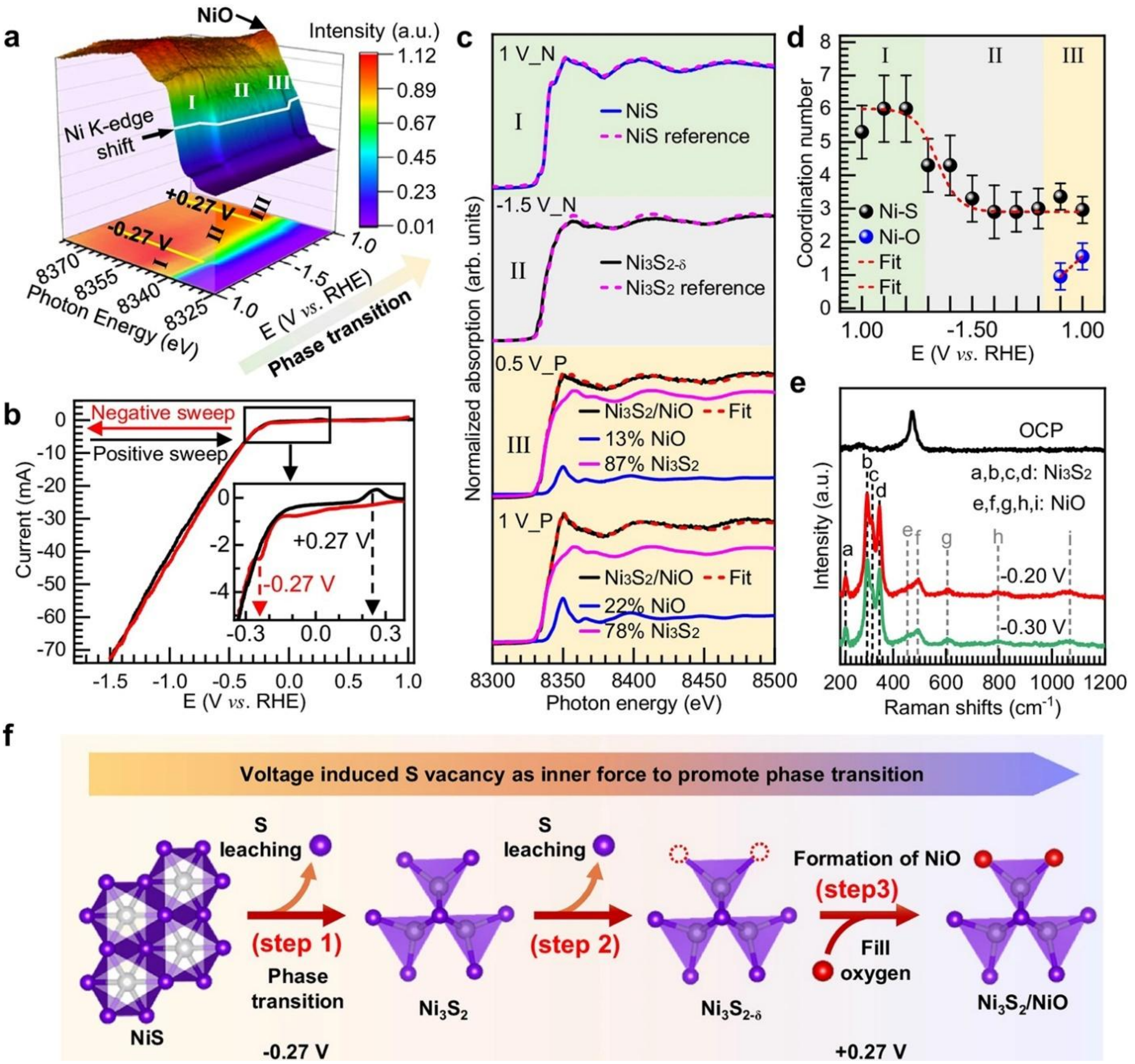

***Figure 1**. (a)* Operando *Ni K-edge XAS for NiS catalyst as a function of applied voltages (Top: 3-dimensional view of Ni K-edge XAS spectra; bottom: 2-dimensional projection from a 3-dimensional view). (b) Corresponding CV profile used for the* operando *XAS measurement (Inset: magnified region marked in the rectangular box). (c) Ni K-edge XAS spectra at specific applied voltages of +1.00, -1.50, +0.50 and +1.00 V (V_N means V in negative sweep and V_P means V in positive sweep of CV) in region I, II, and III respectively, extracted from (a), and their linear combination of Ni_3S_2 and NiO. (d) Coordination number of Ni as a function of applied voltages. (e)* Operando *Raman spectroscopy of NiS at different applied voltages. (f) Illustration for phase transition of NiS catalyst during HER measurement. Reproduced from Ref. [17]*

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative technique able to provide detailed information on the element-specific chemistry and electronic state of the sample [15]. It is one of the most powerful techniques enabling the understanding of the elemental composition and chemical states of the surface of materials [20]. However, the requirement of the ultra-high vacuum condition at the electrode-electrolyte interface challenges the application of *in situ* XPS [15]. This led to the development of the ambient pressure XPS (APXPS), which is also a beneficial tool for the *in-situ* characterization of photoelectrochemical and electrochemical systems [20].

Liu *et al.* [21] used *in situ* and *ex situ* transmission electron microscopy (TEM) in combination with *in situ* XPS to study the encapsulation of metallic iridium nanoparticles (NPs) by carbon in an Ir/C catalyst (Figure 2). The real-time atomic-scale imaging visualized particle reshaping and increased carbon support graphitization upon heating Ir/C in a vacuum. The *in situ* TEM results revealed that carbon overcoating grows over Ir NPs during heating, starting from *ca*. 550 °C. With the carbon overlayers formed, no sintering and migration of Ir NPs is observed at 800 °C, yet the initial Ir NPs sinter at or below 550 °C. The catalytic activity and stability of the encapsulated Ir NPs in the HER were higher than that of the initial (nonencapsulated) state of Ir/C.

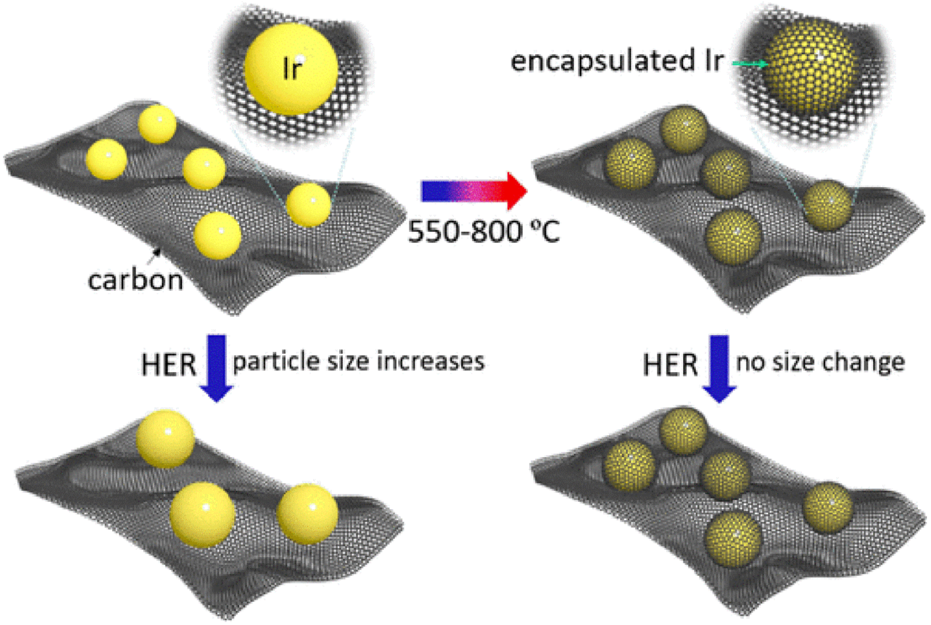

Figure 2. *Carbon encapsulation of supported metallic iridium nanoparticles for HER. Reproduced from Ref. [21]*

X-ray diffraction

XRD is a technique that can monitor the catalyst structural evolution by examining the degree of crystallinity, type of phase structure, and size of crystallite particles [15]. *In situ* XRD analysis was used to study the real-time change of crystal structure during the HER reaction processes [22]. *Operando* XRD has been reported to be a useful tool for the determination of the phase transformation of nanocatalyst for HER [23].

Zhai *et al.* [24] applied *operando* synchrotron X-ray powder diffraction (SXRD) in the $NiSe_2$ electrocatalyst system to reveal an *in situ* phase transformation from cubic $NiSe_2$ to hexagonal NiSe (Figure 3).

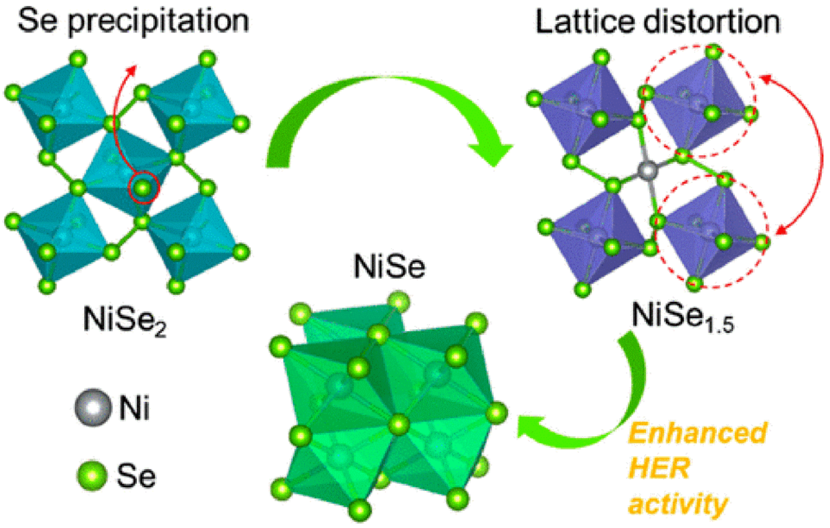

Figure 3. In situ *phase transformation on nickel-based selenides for enhanced hydrogen evolution reaction in alkaline medium. Reproduced from Ref. [24]*

The NiSe phase showed an enhanced catalytic activity and the *operando* Raman spectroscopy was used to verify the decomposition of $NiSe_2$ during HER. This work unravels the underlying phase transition of electrocatalyst on reductive conditions in an alkaline medium and highlights the significance of identifying the intrinsic active sites under realistic reaction conditions.

IR spectroscopy

Operando IR-based techniques are sometimes employed as complementary methods to investigate intermediate species formed on the catalyst surface during electrochemical reactions and to determine the catalytic reaction mechanisms [16]. The *operando* or *in situ* versions of these techniques require fast and highly sensitive detection of target species and have been used to monitor the HER. Two cell configurations, internal and external cell designs, are utilized to perform the in situ/operando characterization of electrochemical reactions using IR-based techniques (Figure 4) [16]. For the internal cell design, a layer of catalyst is deposited over an IR-transparent crystal using electroless or sputtering deposition (Figure 4A), making the catalyst layer thickness limited to a few nanometers, whereas for the external cell design (Figure 4B), the working electrode is positioned close to the prism allowing to achieve the efficient characterization of solution species and adsorbates with a stronger IR illumination and possibility to use different types of electrode materials.

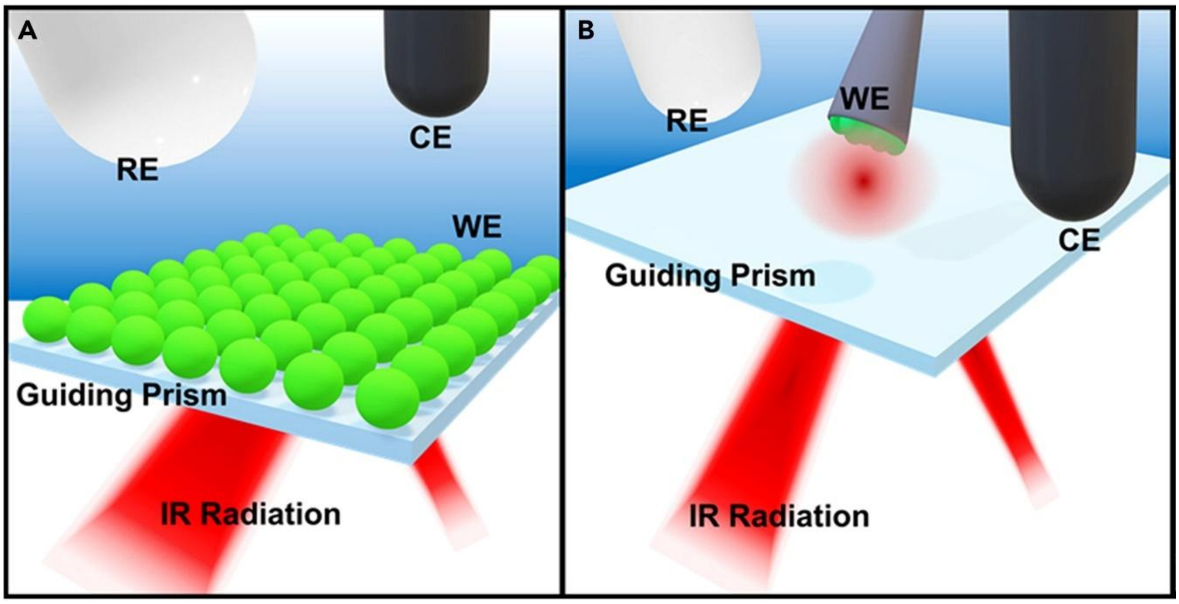

***Figure 4.** Schematic illustration of* operando *IR spectroscopy: (A) Internal and (B) external IR cell designs for* in situ *electrochemical studies. Reproduced from ref. [16]*

Tan *et al.* [25] proposed a practical method for engineering a local acid-like reaction environment to design highly efficient alkaline HER catalysts. By virtue of multiple physicochemical interactions between the substrate, metal active site, and reaction intermediate, they selected Pt/MgO as the prototypical example to construct an acid-like reaction environment in an alkaline medium. *Operando* Raman spectroscopy, synchrotron radiation Fourier transformed infrared spectroscopy (SR-FTIR) spectroscopy and X-ray absorption near-edge spectroscopy (XANES) confirmed the generation of massive amounts of H_3O^+ intermediates on the MgO surface and accumulation around negatively-charged Pt ($Pt^{\delta-}$). This engineered local acid-like reaction environment (in an alkaline medium) led to an extraordinary HER performance with a significantly low overpotential of 39 mV at 10 mA cm^{-2}, much better than the value of 62 mV for 20 wt.% Pt/C and close to the acidic HER behavior of 20 wt.% Pt/C (33 mV). This system also has tenfold higher mass activity than the 20 wt.% Pt/C electrodes in an alkaline medium and 2.5-fold higher than that of 20 wt.% Pt/C in acidic medium at -39 mV vs. RHE. Experimental characterizations and first-principles calculations suggest that the oxygen vacancy-rich MgO is favorable for water dissociation, and the electronic interaction between the MgO and Pt nanoparticles drives electron transfer from VO-MgO to Pt, giving rise to the formation of negatively charged $Pt^{\delta-}$ species. Then, the $Pt^{\delta-}$ accelerates H_3O^+ migration and an acid-like environment is formed around the $Pt^{\delta-}$ in an alkaline medium, thus boosting the HER in this alkaline medium.

Raman spectroscopy

In general, *operando* Raman spectroscopy is performed to identify the active species and reaction intermediate, active site, and phase transitions during the reaction [16]. Thanks to this characterization, the catalyst states, the reaction intermediates, and products during the gas-involved reactions can be detected non-destructively [22].

Zhou *et al.* [26] monitored the origin of MoSe2-electrocatalytic HER activity using the quasi-*operando* XPS and *in situ* Raman spectroscopy. The results clearly revealed dynamic evolution of both Mo and Se species on the $MoSe_2$ electrode surface to promote HER activity and maintain long-term catalytic stability.

Johnson *et al.* [27] utilized the *in situ*/*operando* Raman spectroelectrochemistry (Raman-SEC) combined with density functional theory (DFT) calculations to probe the HER mechanism of the Ti_3C_2 MXene catalyst in aqueous media. In acidic electrolytes, the -O- termination groups are protonated to form Ti-OH bonds, followed by protonation of the adjacent Ti site, leading to hydrogen formation. DFT calculations show that the large overpotential is due to the lack of an optimum balance between O and Ti sites. In neutral electrolytes, H_2O reduction occurs on the surface, leading to surface protonation and hydrogen formation. This results in an overcharging of the structure, leading to the observed large HER overpotential. Bazan-Aguilar *et al.* reported an effortless and low-cost method to obtain highly active Ni foam-based electrocatalysts toward the HER in alkaline media from commercial and low-cost Ni-foam material [28]. The *in-situ* Raman-SEC (Figure 5) and differential electrochemical mass spectrometry achieve a deep understanding of the kinetics and reaction mechanism.

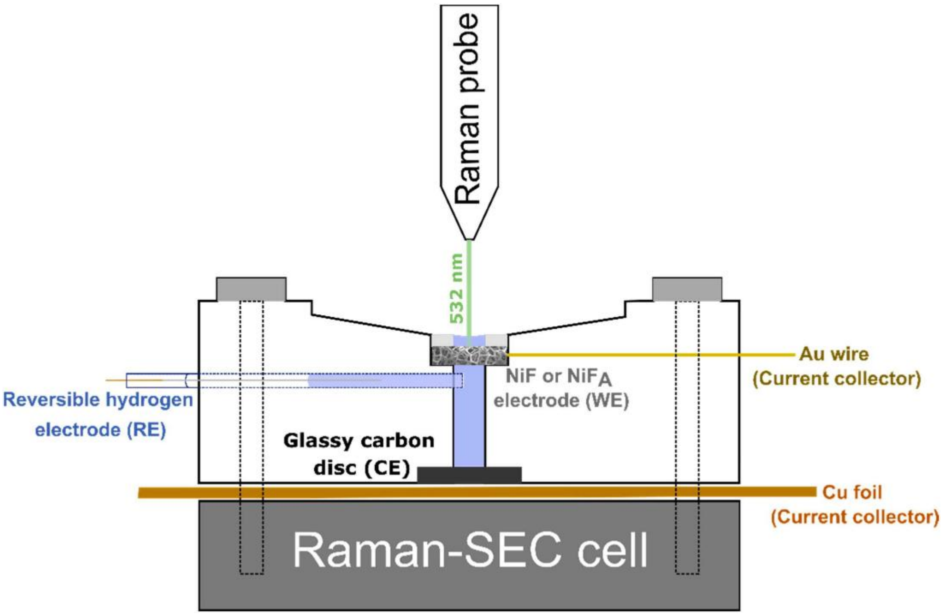

Figure 5. *Schematic illustration of the in-situ Raman spectroelectrochemical cell. Reproduced from Ref. [28]*

Inductively coupled plasma mass spectroscopy

Inductively coupled plasma mass spectroscopy (ICP-MS) is a quantitative elemental analysis technology that detects various elements [20]. This technique has been used to monitor the *operando/ in situ* HER. For example, Aymerich-Armengol *et al.* [29] conducted a comprehensive study on the stability of MoS_2 nanocatalysts under both open circuit potential and HER conditions, with and without Rhenium dopants. This involved a combination of *ex situ* electrochemical degradation and *operando* characterization using SFC-ICPMS (Figure 6). The obtained results were correlated with the evolution of morphology and chemical composition shown by microscopy imaging and spectroscopy at identical locations, XPS, XAS, and calculated Pourbaix diagrams. The *operando* SFC-ICPMS results revealed a stability window from -0.05 to -0.3 V *vs.* RHE for HER operation in sulfuric acid. In addition, the quantitative analysis showed that Re-doped MoS_2 nanocatalysts possess greater stability against dissolution under HER conditions. They also exhibit a wider electrochemical stability window against Re dissolution at anodic potentials, making them more durable for use in acidic electrolyzers compared to pure MoS_2 nanocatalysts.

Coupling of the electrochemical flow cell (EFC) with an ICP-MS device (EFC-ICP-MS) is a powerful method for tracking the online dissolution of metals during electrochemical reactions [30]. It is a powerful electroanalytical technique that provides significant information on the dissolution behavior of the catalysts [31]. It also helps to understand the mechanism of degradation under operating conditions [32,33]. Smiljanić *et al.* monitored the electrochemical stability and degradation mechanisms of a commercial Pd/C catalyst using EFC-ICP-MS [34]. To achieve that, HER was used as a test reaction to observe the corresponding impact of the degradation on the activity of Pd/C. The results of this work emphasized the importance of a systematic study of the durability of Pd nanocatalysts, as this may present a limiting factor for their application in energy conversion devices.

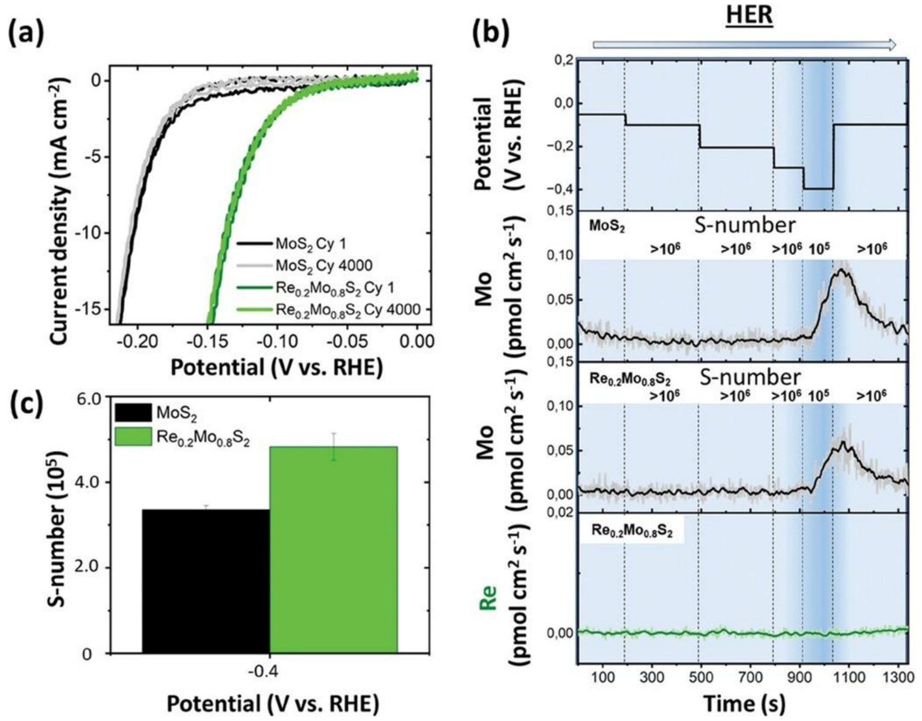

Figure 6. *(a) Cyclic voltammograms comparing the HER performance of MoS_2/CP and $Re_{0.2}Mo_{0.8}S_2$/CP electrodes at cycle 1 and cycle 4000. (b)* Operando *SFC-ICPMS data illustrating the Mo and Re dissolution at different HER potentials. (c) S-number of MoS_2 and $Re_{0.2}Mo_{0.8}S_2$ at −0.4 V_{RHE}. Reproduced from Ref. [29]*

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is one of the effective methods for investigating electrocatalytic reaction kinetics and the properties of the electrode/electrolyte interface [15]. Its *in situ* and non-invasive nature makes it suitable for studying underlying mechanisms and performance under actual catalytic operating conditions [16]. This is the method used in many HER reactions [12,16,35]. For example, Smiljanić *et al.* [30] developed an attractive strategy to suppress Pt dissolution by using an organic matrix tris(aza)-pentacene (TAP) as an alternative support material for Pt. The results of the *in situ* EIS measurements (Figure 7) showed that the improved stability of Pt/TAP was a consequence of the potential-dependent conductivity of TAP support.

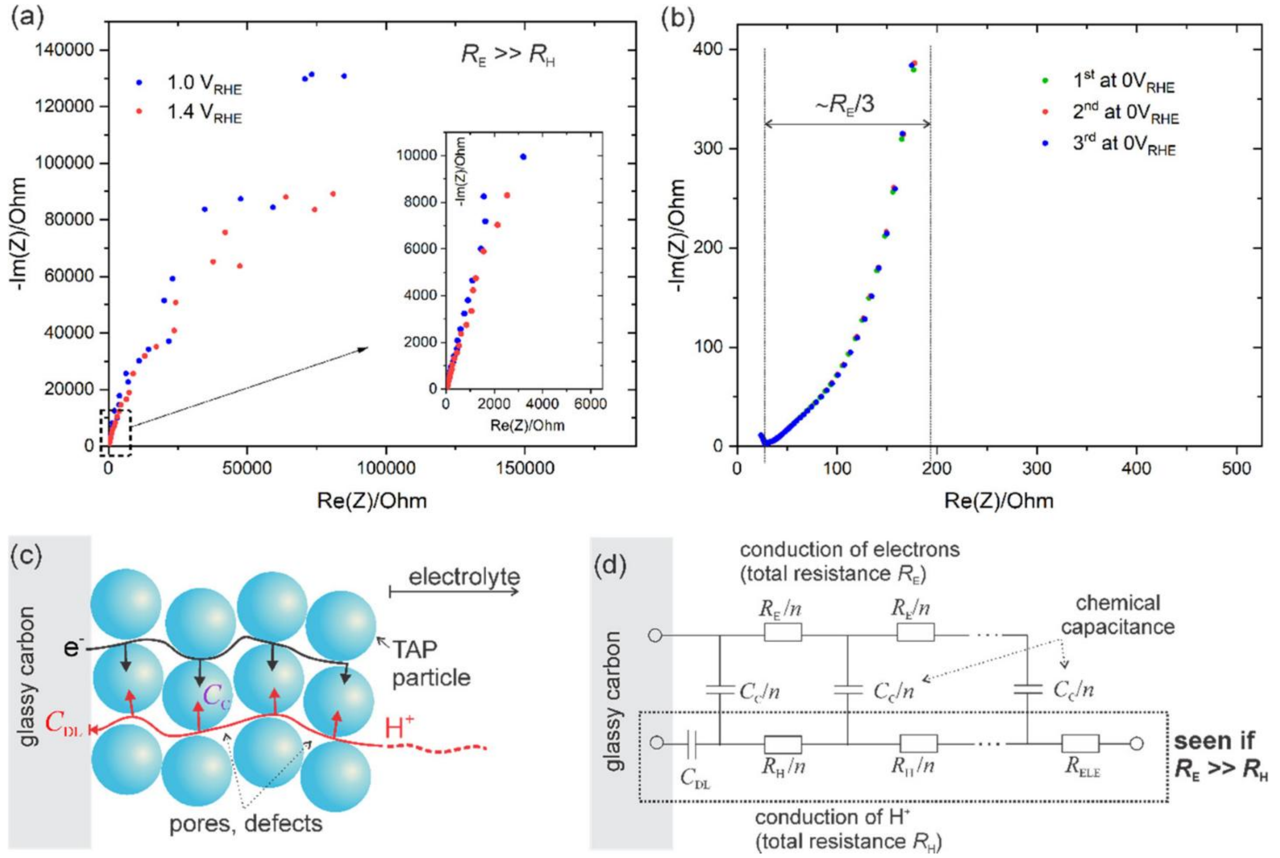

Figure 7. *Impedance spectra measured at (a) high and (b) low potentials vs RHE; (c) Illustration of ionic and electronic transport and insertion in the defect-rich TAP film deposited on a glassy carbon electrode; and (d) transmission line model corresponding to the transport/insertion mechanism(s) in panel (c). Reproduced from Ref. [30]*

Optical microscopy

It has been reported that optical microscopy can be used to investigate the electrolytic HER mechanism. Lemineur *et al.* [36] used interference reflection microscopy (IRM) to probe *operando* an ensemble of individual NPs and the surface gas nanobubbles (NBs) they generate under electrochemical activation (Figure 8). Taking advantage of the high spatial and high temporal resolution of such optical nanoscope, the position of both the nano-catalysts and the NBs are tracked dynamically. In addition, modeling the optical response of gas NBs in the IRM configuration allowed evaluating dynamically the size and shape of the NBs during their production, enabling us to discuss the growth mechanism of gas NBs from single catalytic colloidal Pt NPs. It is shown that the Pt NPs are rapidly electrically disconnected by the NBs, which are still continuously growing.

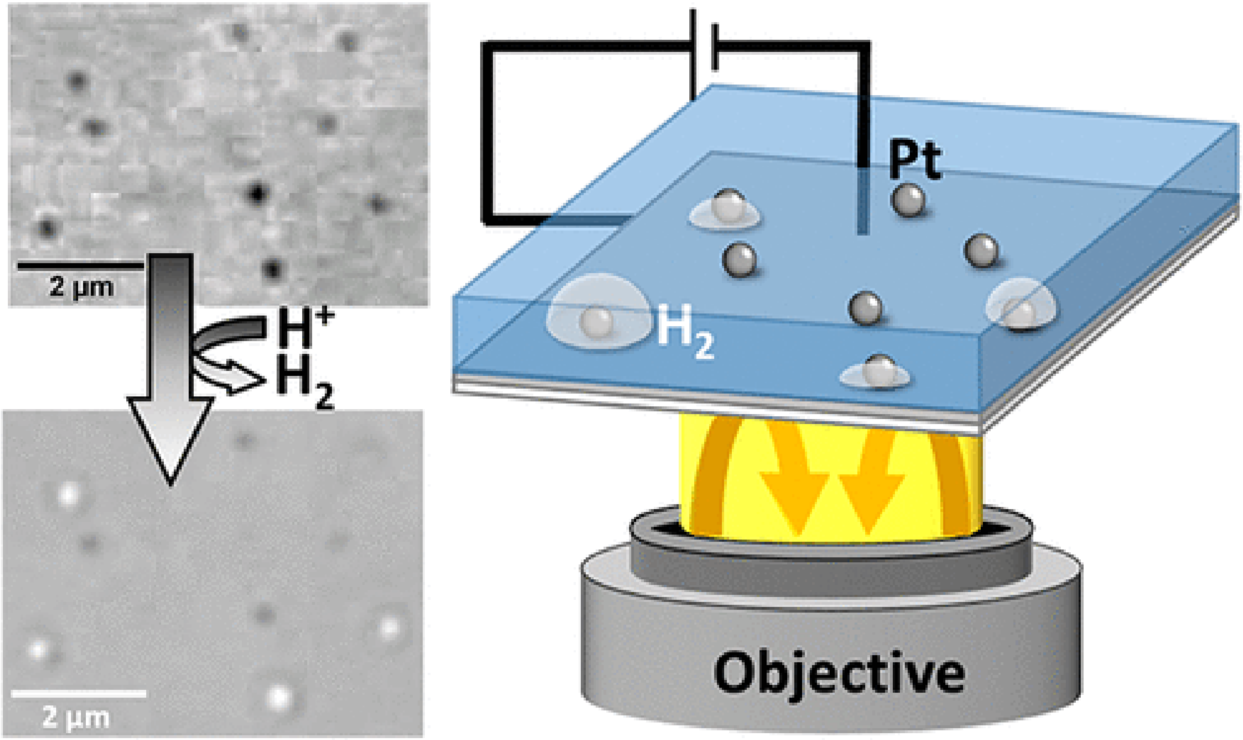

Figure 8. *Imaging and quantifying the formation of single nanobubbles at single Pt nanoparticles during the hydrogen evolution reaction. Reproduced from Ref. [36]*

Transmission electron microscopy

TEM is a technique that combines electron diffraction, imaging, and spectroscopic tools to provide valuable details on the morphology, crystalline structure, and chemical composition of materials [11]. It is used to characterize nanocatalysts, and recently, scientists have shown that it is possible to use it to monitor electrochemical reactions in real time.

In situ TEM is now a fast-growing field of research with numerous possibilities to study samples under applied heat, light excitation, stress, electric or magnetic fields, and electrochemical control [37]. In comparison with other *in situ/operando* techniques, the *in situ/operando* TEM is relatively new, and it helps capture the information of individual atoms or molecules under reaction conditions [38]. It can enhance our fundamental understanding of electrocatalytic processes and catalyst degradation mechanisms in their native environments without the need for freezing or drying the samples [8]. This technique provides the information with atomic, molecular and sometimes nanoscale/microscale resolutions depending on the sample system's nature and the instrumental measurement configuration [38]. It is well-suited to provide unique insights into interfacial electrocatalytic processes, offering nanometer-scale or higher resolution, as well as detailed information on composition and chemical bonding [8]. For HER, a reaction involving a catalyst for liquid reactants, a liquid cell, has been developed to allow the presence of liquid and the potential control of the electrode [38].

Fu *et al.* [39] reported an interesting edge optimization strategy to enhance the catalytic activity of two-dimensional metal phosphorus trichalcogenides (MPTs). With *in situ* reconstructed amorphous surface, MPTs could intrinsically offer better catalytic performance for alkaline hydrogen production (Figure 9). Trace Ru (0.81 wt.%) was doped into $NiPS_3$ nanosheets for alkaline HER. Using *in situ* electrochemical TEM technique, they confirmed that the amorphization process on the edges of $NiPS_3$ is critical for achieving superior activity.

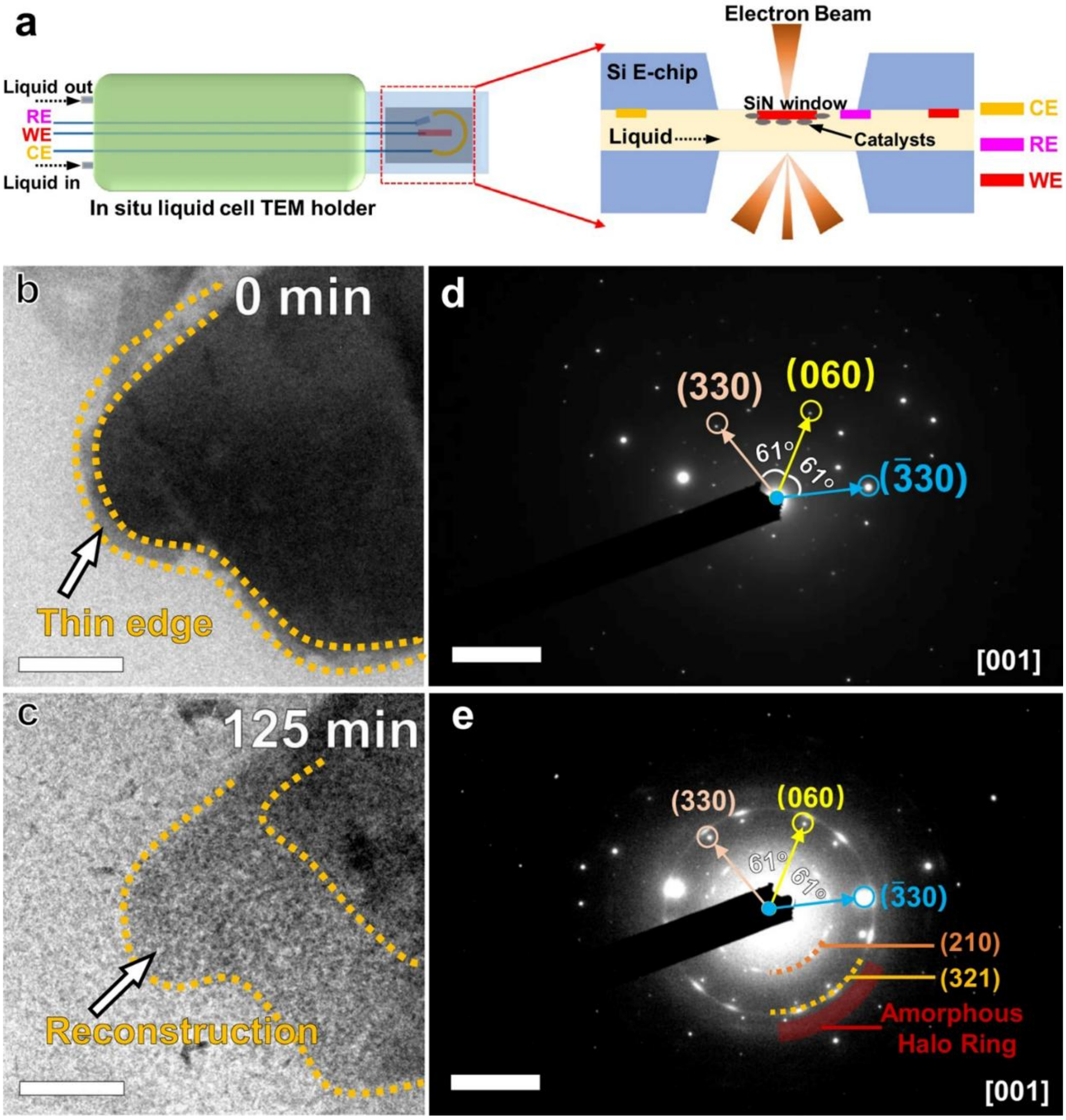

Figure 9. *The structural evolution of Ru-NiPS$_3$ NSs during the HER process: (a) Schematic illustration of the in situ electrochemical liquid cell TEM holder and the liquid cell. In situ liquid TEM image (scale bar: 0.2 µm) of Ru-NiPS$_3$ NSs; (b) before and (c) after chronopotentiometry test; (d), (e) corresponding SAED for (b) and (c), respectively. Reproduced from Ref. [39]*

Electrochemical scanning tunneling microscopy

Electrochemical scanning tunneling microscopy (EC-STM) is another tool providing the information which can help to improve hydrogen production. For example, Kluge *et al.* [40] used electrochemical scanning tunnelling microscopy under reaction conditions (EC-STM) to show that, by using this technique, it is possible to *in situ* visualize the active sites of highly oriented pyrolytic graphite for the HER. This technique was applied to highly ordered pyrolytic graphite in HER conditions. The results showed that at atomic resolution, the most active sites in an acidic medium are located near edge sites and defects, while the basal planes remain inactive.

Lunardon *et al.* reported in details the principles of the EC-STM method, focusing on the HER (Figure 10) [41]. They demonstrated that the quantitative analysis of the noise in the tunneling current allows quantifying the local onset potential and provides information about the microscopic mechanism of electrochemical reactions on sub-nanometric electrocatalytic sites, such as chemically heterogeneous flat interfaces, nanoparticles, and even single-atom defects.

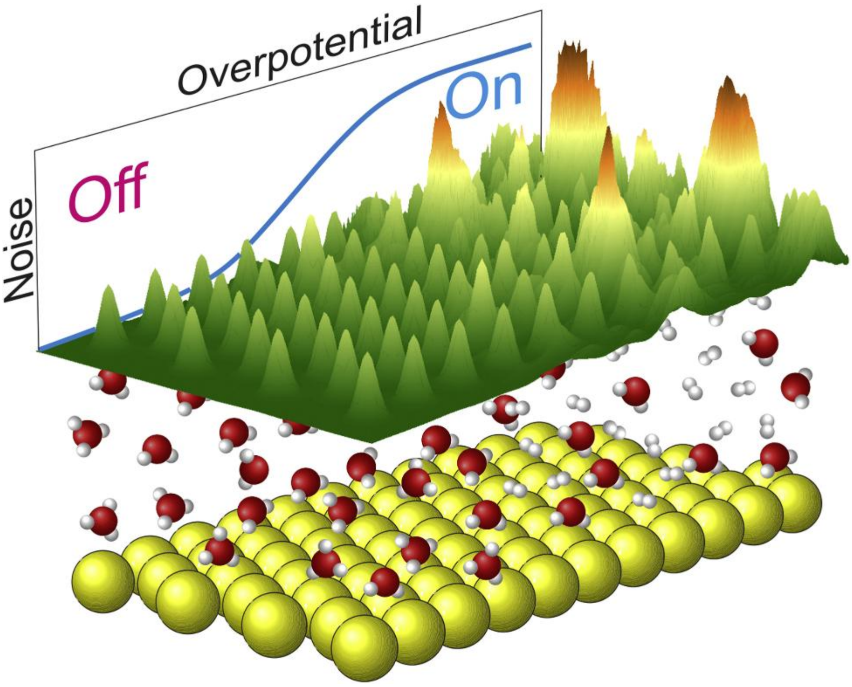

Figure 10. *Monitoring the recorded EC-STM signal noise under reaction condition. Reproduced from Ref. [41]*

Scanning electrochemical microscopy

Scanning electrochemical microscopy (SECM), a technique conceived by Bard and co-workers in 1986, offers unique and powerful functionality for electrocatalysis applications, and its instrumenttation is comparatively simple, inexpensive, and commercially available [8]. The instrumentation of SECM includes a probe (or tip) electrode, a bipotentiostat for independently controlling the potentials of the probe and substrate, micropositioners for scanning the probe in the *xyz* directions, and a computer to manage the system [42]. SECM is able to inspect local topography and electrochemical activity independently and simultaneously while revealing versatility towards a range of different interfaces and experimental conditions [43].

Ciocci *et al.* [44] reported the investigation of the electrochemical behavior of ITO under opto-electrochemical monitoring in scanning electrochemical cell microscopy, SECCM, configuration during the HER in 5 mM of H_2SO_4, a concentration for which the ITO electrode remains stable (Figure 11).

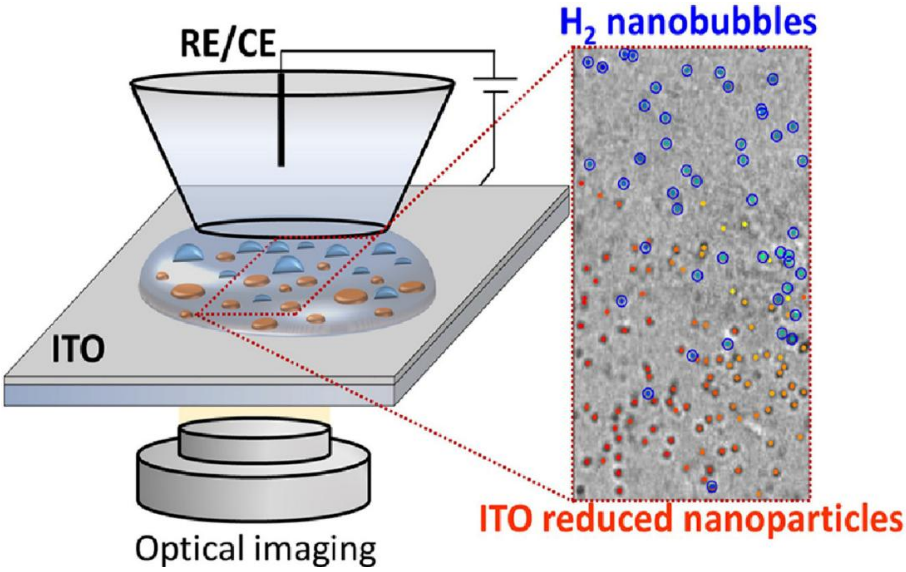

Figure 11. *Differentiating electrochemically active regions of indium tin oxide electrodes for hydrogen evolution and reductive decomposition reactions using an* in situ *optical microscopy approach. Reproduced from Ref. [44]*

The *in situ* optical monitoring through IRM allowed discriminating the formation of H_2 nanobubbles, NBs and the formation of In(0) nanoparticles, NPs, issued from the HER and the ITO electrochemical reduction, respectively. Segregation in electrode potential and space between NBs and NPs formation on the ITO electrode is observed, attributed to the intrinsic variation of the ITO conductivity. That variation was further evidenced by changing the droplet cell position on the ITO substrate and through SECM investigation. Besides, the onset potential of the NPs formation was shifted toward less negative potentials when the conductivity of the ITO increases, whereas the onset potential of the H_2 formation remained mostly unchanged.

Conclusions and future perspectives

HER is an important process in renewable energy conversion and storage systems, including electrolyzers, which transform and store intermittent renewable electricity into chemical energy by generating hydrogen. Researchers are doing their best to find solutions to challenges hindering the competitive commercialization of hydrogen energy. One of the ways to achieve this is to exploit the advantages of the *operando*/*in situ* characterization techniques. This has shown good progress, and research is still being done.

Recently, machine learning and artificial intelligence have been used to find the solutions to the problems we encounter and even improve technology. Their incorporation in the studies on monitoring nanocatalyst-based electrochemical HER will accelerate successful hydrogen energy production and commercialization. The miniaturization of the characterization equipment is another important parameter in this field. Volatile electrolytes disturb the functioning of some characterization instruments, *e.g.* they lead to the poor special resolution and contrast of TEM [45]. The consideration of the reduction of the radiolysis of water, attempting electrode preparation methods, using compressive sensing software, exploration of various electrolytes, minimizing the electron beam induced damage, and controlling the liquid film thickness, may lead to the solution. In addition, the integration of multiple *operando*/*in situ* techniques is suitable as one technique cannot provide all the necessary information. Also, the combination of theoretical calculations and experimental studies will contribute more. The integration of machine learning algorithms and automated data analysis for large data sets will bring much improvement [46].

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