A primer to *in-situ* opto- and spectro-electrochemistry
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**Abstract**

Electrochemistry is promising to study interfacial electron transfers and redox reactions, but its lack of access to molecular structural information limits understanding on complicated systems. Complementary optical and spectroscopic measurements *in situ* become necessary to visualize the electrochemical processes, providing the electronic and structural identification of the reactants and products. Recent advancement in instrumentation and nanostructures has enabled spatiotemporal resolution of molecules during complex reactions, opening opportunities to optically reveal intermediates, mechanisms, and rates, as the keys to fundamental and theoretical electrochemistry. This short review introduces the latest optical and spectroscopic techniques that are feasible for electrochemists to start with, including dark-field, Raman, infrared, and ultraviolet-visible-near infrared opto- and spectro-electrochemistry.

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**Keywords**

Opto-electrochemistry, Spectro-electrochemistry, Spectroelectrochemistry, Optical microscopy, Imaging, Dark-field, Raman, IR, UV-Vis-NIR, Spectroscopy.

**Introduction**

Using light-matter interaction to visualize charge transport is powerful to gain as much information as possible about a molecule. *In-situ* opto- and spectro-electrochemistry coupling electrochemical measurements with optical and spectroscopic characterizations is an emerging tool to fulfill this objective. Recently, a number of valuable reviews cover different aspects of opto- and spectro-electrochemistry. Sojic and Bouffier reported the optical imaging of electrochemically induced fluorescence and electrochemiluminescence [1]. Noël and Lemineur demonstrated the optical microscopy to study single nanoparticles impact [2]. Sharma et al. summarized the use of X-ray and neutron scattering to study electrochemical energy storage devices [3]. Ren et al. focused on the electrochemical plasmon-enhanced Raman spectroscopy [4–6]. Fontanesi et al. highlighted the importance of synergy between electrochemical, spectroscopic, and theoretical methods [7]. Odijk et al. described spectro-electrochemical techniques in detail with an overview of the cell configurations [8].

This mini review aims to provide electrochemists with a quick guide to choose the right optical and spectroscopic technique to suit the molecules and purposes. Here, vibrational spectroscopy comprised of infrared (IR) absorption and Raman scattering will be introduced to detect the changes of chemical bond and molecular structure during the redox of a molecule. While the spectrum corresponds to the fingerprint molecular structure, each band can be assigned to the vibrational mode of a certain chemical bond or functional group. Electronic spectroscopy, namely ultraviolet-visible-near infrared (UV-Vis-NIR) absorption, will also be introduced to probe the changes of electronic structure during the redox process. Further, dark-field (DF) scattering microscopy and spectroscopy will be introduced to monitor the changes of electronic state for particle-based electrochemistry. However, the order of techniques in discussion will be different considering the set-up of instrument. Microscope for DF imaging is often integrated with DF and Raman spectroscopy as the optics for excitation and detection are in the visible region, which will thus be elaborated first. IR spectroscopy, as the complementary technique to Raman, will then be explored. UV-Vis-NIR spectroscopy, as the more mature and widely used technique, will be covered last. The latest research will be used as examples to showcase how opto-/spectro-electrochemistry can serve mechanistic understanding on molecule redox.

**Dark-field microscopy and spectroscopy**

Dark-field (DF, see setup in Figure 1a, [9]) microscopy can provide real-time optical visualization of particles at nano- to micro-meter scale undergoing dynamic reactions triggered by a suitable electrochemical potential.
Particles are illuminated in a way that only scattering light is collected, yielding high contrast images. Indirectly, Compton used the oxidation of acid precursor to decrease pH near the working electrode, driving the dissolution of CaCO₃ at the single marine phytoplankton cell (Figure 1b). Through observation in DF imaging, dissolution rates and cell size effect were derived to monitor the ocean calcification, which is vital for the carbon cycle [10-12]. Directly, Tschulik observed the silver nanoparticles dissolution in DF imaging [13]. Faez modulated the applied potential at a rough surface and recorded the scattering intensity from DF imaging to study the restructuring of electrical double layer (EDL) [14].

DF spectroscopy is extensively employed to study redox-active molecules functionalized in plasmonic nanostructures. The peak position and linewidth of a DF spectrum depend on the resonance energy, composition, size, morphology, the refractive index of the surrounding medium. To determine these parameters, finite-difference time-domain (FDTD, by Lumerical software) calculation is often carried out to simulate the experimental DF spectra [15,16]. Baumberg fabricated a metafilm with color dynamics for flexible devices by encapsulating gold nanoparticles (AuNPs) with a conductive polymer shell. DF imaging and spectroscopy (Figure 1c, d) show the electrochromic tuning based on the refractive index change with polyaniline redox state [15]. Landes demonstrated the photo-electropolymerization on gold nanorods (AuNRs) in DF spectra (Figure 1e, f), which are simulated to determine the plasmon energy transfer [16].

To maximize the collection efficiency not only for DF but also for the add-on spectroscopies, we can optimize the design for electrochemical cell and microscope. First, if...
collection is from top of the cell (see Graphical Abstract), the optical path length can be reduced by minimizing the distance between coverslip and working electrode, only allowing a thin-layer of electrolyte in between. Second, if collection is from underneath (i.e. inverted microscope, Figure 1e), a transparent (e.g. a thin film of Au, Pt, or indium tin oxide) or mesh working electrode (Figure 4a, to let light go through) can be placed at the bottom of the cell, so thin-layer is no longer needed. Third, an oil-immersion objective can be used to contact the coverslip (Figure 1e) or a water-immersion objective to dip into the electrolyte (Figure 1g). Without such an immersion objective in the conventional setup, light travels through electrolyte, glass coverslip, air, and into the microscope causing image distortion (like viewing underwater objects from above). Refractive index of oil is similar to glass, and it is nearly the same between water and electrolyte, making the immersion objectives efficient in collecting scattered light. Ren showed the improved sensitivity in DF imaging and spectroscopy (Figure 1h–k), enabling the observation of atomic layer electrodeposition on single crystal surface [17].

**Raman spectroscopy**

According to the selection rule for vibrational spectroscopy, for a mode to be Raman active, there must be a change in polarizability of the molecule. Chemical bonds and functional groups such as aromatic rings, alkene (C=C), amide (O=C-N), nitro group (C-NO₂), nitrate (NO₃⁻), carbonate (CO₃²⁻), chlorate (ClO₄⁻), sulfate (SO₄²⁻), and phosphate (PO₄³⁻) give high signal-to-noise ratio (SNR) Raman bands in the fingerprint region (400-1800 cm⁻¹). High SNR means lower laser power and shorter integration time is required, which is important for tracking reaction dynamics. Euser embedded a hollow-core optical fiber inside a Li-ion battery (Figure 2a) to measure the Raman spectra of the solvent (EC in Figure 2d) and electrolyte additives.

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**Figure 2**

Raman and surface-enhanced Raman spectroscopy with electrochemistry. (a) Schematic of hollow-core fiber embedded in the pouch cell, and the Raman spectra during charge and discharge process showing three modes of battery electrolytes (d, h–i). Reprinted from [18], copyright 2022 Nature Publishing Group. (b) Schematic of the ‘molecular ruler’ for electrical double layer using viologen self-assembled monolayers (SAMs) at different lengths. (c) Resonance Raman spectra (RRS) of SAMs on Au(111) at −0.7 V (vs. SCE). Reprinted from [23], copyright 2020 American Chemical Society. (e) Schematic of nanoparticle-on-mirror (NPOM) geometry for surface-enhanced raman spectroscopy (SERS) to study electrocatalyst redox, detect intermediate (structure 2w and 4b), and determine reaction mechanism. (f) SERS of reaction intermediate at −0.8 V (vs. Ag/AgCl). Adapted from [21]. (g) 3D finite-difference time-domain (FDTD) simulation of electric field near shell-isolated nanoparticles (SHINs). (h) SHIN-enhanced Raman spectroscopy (SHINERS) of interfacial water on Pt(111) at different potential applied. Gaussian fits of three O-H stretching modes in blue, orange, and red, showing different number of hydrogen-bonds coordination on water. Reprinted from [22]. e-h copyright 2021 Nature Publishing Group.
(VC). Through analysis of EC ring breathing mode and VC vinylene (HC=CH) band during cycling, Li-ion solvation dynamics can be tracked to study the degradation mechanism [18]. The vibrational frequencies of alkyne (C≡C), nitrile (C≡N), and carbon monoxide (C≡O) sit in the silent region (2100-2300 cm⁻¹) and are sensitive to the electric field. This is known as the vibrational Stark effect and can be used to probe the local field at the molecule by both Raman [19] and infrared [20] spectroscopy (see below). With supported density functional theory (DFT, by Gaussian software or Vienna ab initio simulation pack) calculations, complicated systems can be identified, such as the quantification of Stark shift in the EDL [19], reaction intermediate, and mechanism of organometallic complexes (Figure 2e, f) [21], and the structure of multiple hydrogen-bonds coordinated water (Figure 2h) [22].

Raman scattering is very weak (∼10⁻⁶% of incident light) but can be strongly enhanced (by > 10⁵) in two ways. First, when the excitation laser lies within the electronic absorption of a molecule, molecular resonance occurs giving resonance Raman spectroscopy (RRS). Li used viologen self-assembled monolayers (SAMs) with different alkyl chain length to probe the electric field in the EDL (Figure 2b). This is achieved by generating RRS (Figure 2c) of the mono-reduced radical cation of viologen (V⁺⁺) under 638 nm laser illumination [23]. Second, when the excitation laser matches with the resonance energy of a plasmonic nanostructure, electromagnetic field enhancement occurs. One such approach is tip-enhanced Raman spectroscopy (TERS), but it is not elaborated here due to the challenge of reliable tip fabrication and maintenance. The alternative approach is surface-enhanced Raman spectroscopy (SERS), which is...
easy to implement via enhancement from roughened surface [24], alloy nanoparticles aggregate [25], nanoparticle-on-mirror (NPoM, Figure 2e) geometry [19,21], and shell-isolated nanoparticles (SHINs, Figure 2g) [22,26]. Among these methods, NPoM and SHINs have a uniform field in the gap between the nanoparticles and the substrate, enabling the quantification of molecules from spectral intensity.

**Infrared spectroscopy**

Following the selection rule, for a vibrational mode to be infrared (IR) active, there must be a change in the dipole moment of the molecule after the absorption. IR spectrum is measured in the region of 4000–600 cm⁻¹. Molecules such as water (H₂O), methane (CH₄), hydrogen chloride (HCl), nitric oxide (NO), nitrous oxide (N₂O), and chemical bonds such as C=O, C-H, N-H, O-H, give high SNR in IR spectra. C≡C, C≡N, and C≡O give both IR and Raman bands in the silent region, so they can be easily detected (see vibrational Stark effect above). DFT calculations can also be used to simulate IR spectra to extract information from the system [20]. Since water has strong absorption bands in IR spectra, attenuated total reflection (ATR) configuration is typically used for electrochemical cells (Figure 3a), where light hits the sample at a certain angle that total reflection happens. An evanescent wave is created, which only penetrates the first micro-meter of the solution adjacent to the working electrode, minimizing the signals from water. Like SERS, IR absorption can also be enhanced through surface-enhanced infrared reflection absorption spectroscopy (SEIRAS). Lipkowski measured ATR-SEIRAS of interfacial water on the alloy electrode (Figure 3b), and found the water structure is in both forms of monomers and clusters of molecules [27]. Waegele compared ATR-SEIRAS of C≡O on terrace and at defect sites of rough copper surface (Figure 3c), and the different Stark shift indicated different effective potentials at the two morphology [28]. Hildebrandt used C≡N as the Stark probe to determine the local electric field at the pure SAM, mixed SAM with lipid bilayer, and pure bilayer. The relationship between the electrode potential and the potential across the membrane is understood [29]. To speed up data collection, Fourier-transform infrared

**Figure 4**

**Ultraviolet-visible-near infrared spectroscopy with electrochemistry.** (a) Photograph of the boron-doped diamond (BDD) mesh electrode and the 3D printed cell. (b) UV-Vis spectra of anthraquinone-2-sulfonate (AQS) and its electrochemically reduced state, anthrahydroquinone-2-sulfonate (AH₂QS). Reprinted from [38], copyright 2022 Royal Society of Chemistry. (c) UV-Vis spectra of hydrous iridium oxides (IrO₃) upon oxidation, to identify redox states involving Ir⁶⁺, Ir⁵⁺, Ir⁴⁺, and Ir³⁺ in (e). Reprinted from [32], copyright 2021 American Chemistry Society. (d) Proposed mechanism for CO₂ electro-reduction by a molecular cobalt phthalocyanine catalyst with four phosphonic acid anchoring groups (CoPcP) from its UV-Vis spectra in (g). Reprinted from [35], copyright 2021 American Chemistry Society. (f) UV-Vis spectra of triphenylamine- and BN-substituted coronene diimide (TPA-BNCDI) upon oxidation. (h) Structure of TPA-BNCDI. Adapted from [39], copyright 2021 Royal Society of Chemistry. (i) Schematic of a screen-printed electrode (SPE), optical fibers at two sides for UV-Vis spectroscopy, and Raman spectrometer in the middle. (j) UV-Vis and (k) Raman spectra of K₄[Fe(CN)₆] solution on a Pt-SPE. Reprinted from [40], copyright 2022 Springer.
(FTIR) spectroscopy is also used for electrochemistry. Unlike conventional IR spectroscopy, where the sample is irradiated with different single wavelengths (dispersive), FTIR collects the spectra of all wavelengths simultaneously. Koper obtained FTIR of simple monosaccharides during their reduction on Pt and Pd electrode (Figure 3d,e) to reveal the reaction pathways (Figure 3f) [30]. Stripp recorded ATR-FTIR of a metalloenzymatic complex found in bacteria and algae, [FeFe]-hydrogenase (Figure 3g), during its catalytic hydrogen evolution reaction to derive the proton transfer pathway and reaction mechanism [31].

Ultraviolet-visible-near infrared spectroscopy

Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy was one of the first spectro-electrochemical techniques dated back to 1960s, but it is still in active use for photocatalyst studies. UV-Vis-NIR spectroscopy can be applied to detect changes in the electronic structure (i.e. color changes) of a molecule during redox (Figure 4c,e) [32,33], protonation/deprotonation [34], ligand coordination/dissociation (in organometallic complexes, Figure 4d,g) [35], or polymerization [36]. Either transmission or reflection can be collected in the range of 135–3300 nm, and used for quantitative analysis.

UV-Vis-NIR spectra can be analyzed with DFT or time-dependent density functional theory (TD-DFT, by NWChem package) calculations to derive information such as electronic transition, steady state, and HOMO-LUMO band-gap (energy difference between a molecule’s highest energy occupied molecular orbital and its lowest energy unoccupied molecular orbital). Fontanesi characterized the electroreduction mechanism of halogenated naphthalene derivatives by integrating UV-Vis spectra and DFT calculations [37]. Stavros used boron-doped diamond (BDD, Figure 4a) mesh electrode to avoid interference from a dissolved oxygen reduction signal for the study of an oxidative photocatalyst, anthraquinone-2-sulfonate (AQS, Figure 4b). Through the combination of redox UV-Vis spectra, ultrafast transient absorption spectra, and TD-DFT calculations, AQS lifetime and relaxation mechanism was resolved [38]. Staubitz reported how electronic properties are tuned by substituting C/C with B/N atoms. Through redox UV-Vis spectra of the BN-substituted molecule (TPA-BNCDI, Figure 4f, h) and TD-DFT computations, an intramolecular photoinduced electron transfer unique to these substituents was discovered [39].

It is worth noting that Colina combined UV-Vis and Raman spectroscopy (Figure 4i–k) by integrating screen-printed electrodes with optical fibers at two sides for UV-Vis spectroscopy, and collection path in the middle for Raman spectroscopy, both using portable spectrometers [40].

Conclusions and perspectives

The synergy of electrochemical, optical, and spectroscopic techniques has been successful evidenced by the extensive publications on electrocatalytic carbon dioxide reduction reaction (CO2RR), carbon monoxide oxidation reaction (COOR), hydrogen/oxygen evolution reaction (HER/OER), and oxygen reduction reaction (ORR). As a future perspective, opto- and spectro-electrochemistry is ready to take the challenge to explore systems with more complicated molecular and electronic structures. With accessibility to 3D printing technology, electrochemists can design cells adapted to commercially available microscopes and spectrometers, or even portable devices, easing the need to home-build optics to fit the conventional cells. With the development of plasmonic enhancement in spectroscopy (SERS and SEIRAS) and imaging [41,42], as well as careful choice of technique suitable for the molecule and purpose, high SNR can facilitate the monitoring of reaction dynamics. Supported with various theoretical and computational calculations, spectra and images can be translated into molecular or electronic structure, reaction mechanism and kinetics. Hence, the spatiotemporal resolution of molecules during reactions can be achieved. Further, we can invite stimuli such as varying laser power illumination [43], NIR/IR/UV pumping [44], and magnetic field [45,46] to see how they influence molecule redox and interfacial electron transfer process. Opto- and spectro-electrochemistry based on microfluidic chips [47], capacitance imaging using complementary metal–oxide–semiconductor (CMOS) [48], and imaging of dielectric materials using interference reflection microscopy [49,50] are also very interesting directions. Optical and spectroscopic techniques have and will continue to aid the fundamental understanding of electrochemistry, improving the performance of catalysis, sensors, molecular electronics, and metamaterials.

Declaration of competing interest

The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

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Acknowledgments

The author acknowledges the 3D drawing of graphical abstract by P. N. van der Velde, appreciates the financial support for her tenure track from the University of Twente, the Netherlands, and gratefully thanks R.G. Compton, J. J. Baumberg, P. Matousek, and C. A. Nijhuis for their endless support.
References

Papers of particular interest, published within the period of review, have been highlighted as:
* of special interest
** of outstanding interest


Demonstration of how ultraviolet-visible spectroelectrochemistry is combined with time-dependent density functional theory calculation to unravel the reaction mechanism of anthaquinones.


Demonstration of commercially available portable devices combining Raman and ultraviolet-visible spectro-electrochemistry.


