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Molecular Electrochemistry. An overview of a cross-field integrated approach.

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Abstract

This review summarizes the essential results in molecular electrochemistry achieved by a synergy of electrochemical, spectroscopic, and theoretical state-of-the-art. A number of selected case studies are reported, where such a synergetic approach enabled drawing a complete picture of various hybrid experimental systems. In these complex assemblies, electrochemical behavior is rationalized at a molecular level, where the electroactive molecular species is adsorbed or in tight contact with the working electrode. Finally, the relevance of the combined experimental and theoretical tactic in solid-state electrochemistry, a territory amidst novel concepts for solid-state electronics, is recapped.

1) Introduction

Electrochemistry is a compelling and wide-spectrum discipline, maybe the foremost example of interdisciplinary science. It spans from the study of fundamental aspects related to adsorption at the electrode/solution interface, eventually featuring charge transfer processes to applicative analytical aspects (detectors & sensors systems) and synthetic related applications (electrocrystallization), with immobilization within a polymer matrix [1–3], electrocatalysis, and corrosion-related phenomena [4,5]. One should not omit the importance of bio-electrochemistry in life science, from the legendary work of Luigi Galvani [6] on frogs (which is indeed the birth of electrochemistry) to scientific journals dedicated explicitly to bioelectrochemistry [7]. Eventually, electrochemistry plays a special role (which is inevitably going to grow more and more important) in energy storage: the battery arena [8,9]. Anyhow, electrochemistry is able to shed light on complex processes at the molecular scale, for instance, allowing to determine the size and to assess the molecular orientation of a single electroactive species adsorbed on the electrode via surface tension measurements (Lippman) and electrodesorption experiments [10]. This is miraculous as it relies on the measurement of the basic macroscopic parameters: the current and the potential. Especially when dealing with reaction mechanisms, implementation of non-electrochemical experimental techniques integrated into an electrochemical system provide complementary/independent data sensitive to “molecular” properties of electroactive species and transient/reaction intermediates. Quite often, spectroscopic techniques are coupled with electrochemical measurements in quite elaborate and complex setups. UV-Vis electronic and vibrational (IR and Raman) techniques are the most diffused in combination with both “in-situ” or “ex-situ” electrochemical experiments. Also, much more demanding experimental arrangements have been implemented, such as i) X-ray scattering techniques (SAXS, GISAXS) and photoelectron spectroscopies implemented on synchrotron beamlines [11–15] or electron paramagnetic resonance (EPR) [16–18]. Eventually, not so diffused nuclear magnetic resonance (NMR) and second harmonic generation (SHG) “in-situ” measurements, till to finish with kind-of-esoteric 3D (Hall potential measurement) spin-dependent electrochemistry [19]. Within this context, the availability of theoretical indices allows us to deepen further, extend and probe the mechanisms present in complex electrochemical systems. Thus, the synergy of conventional electrochemical experiments, the complementary synergetic approach opens the door to exploration and understanding the hidden aspects of the electrochemical processes beyond a traditional experimental frame. [16,20–23] The most significant demonstrations are summarized herein.

2) Electroactive complex molecular architectures

In the molecular electrochemistry cross-field, a major role is played by hybrid systems, where a suitable reversible redox-probe is grafted on a conductive surface or embedded in a well-defined molecular architecture. Two examples of such hybrid systems are worth mentioning. The excellent work of Kumar et al. reports on a well-ordered cascade monolayer featuring two reversible redox couples, Os(II) and Ru(II), grafted on a Si(100)/ITO-functionalized electrode [24], while the study by Maran et al. discusses the reversible behavior of Au nanoparticles in dendrimer-like superstructures (see Figure 1).[25] Remarkably, both works relate the change in the oxidation state of the metals (as a function of the potential) to the electronic state probed by measuring the UV-Vis spectra. Indeed, the vast majority of electrochemical studies pay attention to i) structural characterization of the electrode/solution interface or the complex redox-probe/encapsulating system, and ii) the rationalization of the charge transfer kinetics and dynamics, as a function of the overall structure (in terms of both molecular properties of the single building-blocks elements and order). Proper elaboration of the electrochemical behaviour (for instance, cyclic voltammetry (CV) and impedance spectroscopy (EIS) measurements and simulations) allow for a first assessment of structural characteristics. Anyhow, the cross-check of a reasonable hypothesis, inferred by the discussion of the electrochemical evidences, carried out by using an independent technique is desirable. In this vein, the concerted efforts of spectroscopic and theoretical tools play a major role in the paradigm shift in understanding the electrochemical processes down to the molecular level.

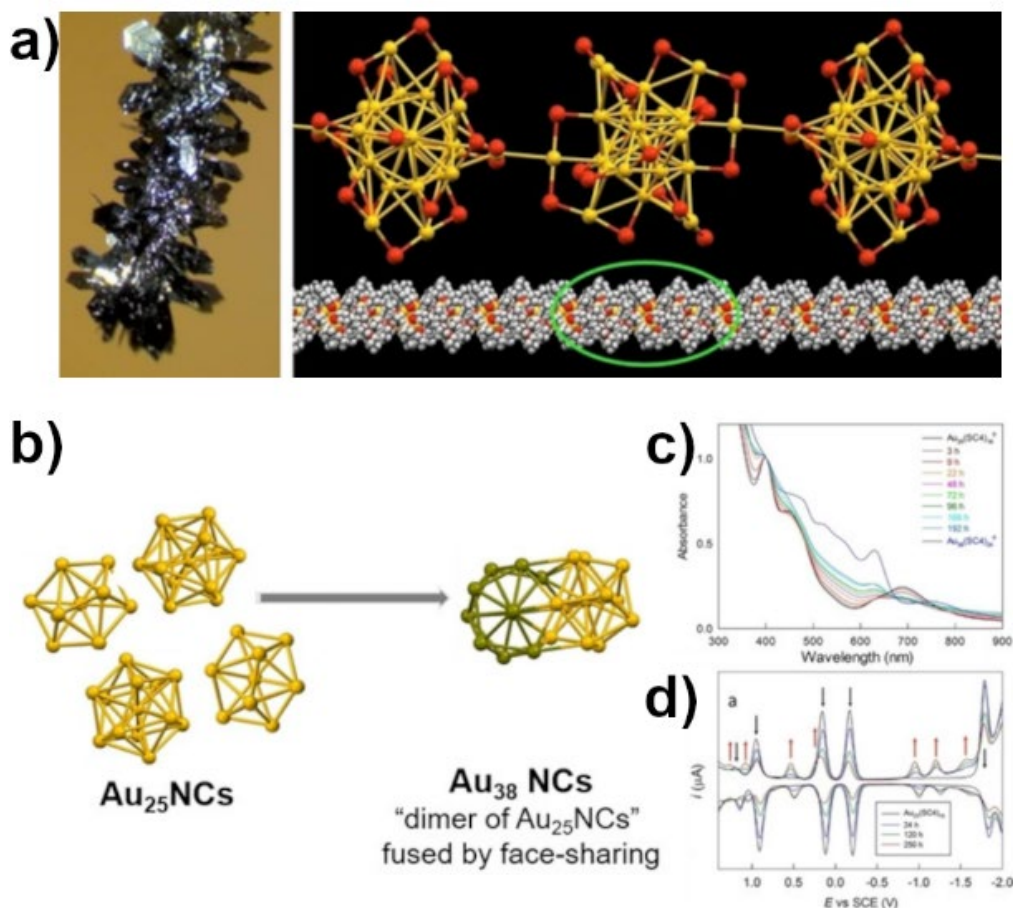


Figure 1. a) Electrocrystallization of $\text{Au}_{25}(\text{SR})_{18}^0$ crystals covering the gold wire electrode extracted from the electrochemical cell at the end of the electrolysis (left). Schematic representation of the electrocrystallized Au nanocrystals (right); b) Illustration of the Au nanocrystals bimolecular fusion to $\text{Au}_{38}(\text{SR})_{24}$; c) UV/Vis absorption spectra samples taken during the fusion of $\text{Au}_{25}(\text{SBu})_{18}^0$; d) differential pulse voltammetry curves of samples during the fusion. (Reprinted with permission from [25]. © 2020 Wiley-VCH GmbH)

3) “In-situ” spectro-electrochemistry (SEC)

Vibrational spectroscopy is a classical tool and a natural first-choice when dealing with molecular systems. The most common vibrational spectroscopic techniques are IR absorption and Raman scattering. With different selection rules, both probe the vibrational fingerprints of the molecular structures and intermolecular interactions on the level of individual molecules, functional groups, and their fragments. Vibrational spectroscopy shows several advantages for the characterization of complex matter as it is a non-destructive method, capable of in-situ and time-dependent addressing different research problems in the industrial quality control, reaction mechanisms, cultural heritage.[26–29] Vibrational spectroscopy is also used for the ex-situ studies of electrochemical processes in thin films or even monolayers with the advantage of the signal enhancement exploiting the surface plasmon resonance in the Raman scattering

process (SERS – surface-enhanced Raman spectroscopy) or in phase modulation in the combined infrared reflection absorption configuration for IR spectroscopy (PM-IRRAS). Nevertheless, robust theoretical feedback is needed to complete the full picture of a particular process. For example, a combination of the electrochemical and spectroscopic “ex-situ” probes proved to be effective in clarifying the structural properties of a thiophene polymer grown on glassy carbon, in tight comparison to the theoretical calculation of the Raman spectra. [30,31] Recently the study of electrochemical processes at the interfaces attracted significant interest in the scientific community. Indeed, the charge-discharge occurring at the electrode interface in batteries represents a typical example of such a process. Therefore, fundamental studies providing a strategy for a precise determination of the detailed mechanism at a molecular level represent a crucial step forward for developing more efficient alternatives for energy storage. In this context, implementing the vibrational spectroscopy know-how for in-situ investigation of the electrochemical processes occurring at the electrode interface is of utmost importance. Immense progress in experimental design and instrumentation has been made lately. In the attempt to utilize in-situ IR spectroscopy with conventional electrochemical techniques, several challenging tasks need to be overcome to study the phenomena at the solid-liquid interface. Indeed, the fundamental issues are associated with signal-to-noise ratio: i) interference by solution electrolyte species; ii) low reflection of the radiation at the electrode surface; iii) weak signal from the monolayer adsorbed species on the electrode surfaces. To minimize the IR absorption by the electrolyte, two approaches towards the cell design have been applied using the internal and external reflection configurations, see Figure 2. In the external reflection configuration, a very thin electrode is used. The attenuated total reflection (ATR) prism is placed in contact to ensure the shortest path length through the liquid. In these conditions, the signal from the electrode-electrolyte is maximized, and the detection of both adsorbed and in-solution species involved in the electrochemical process is achieved.[32]

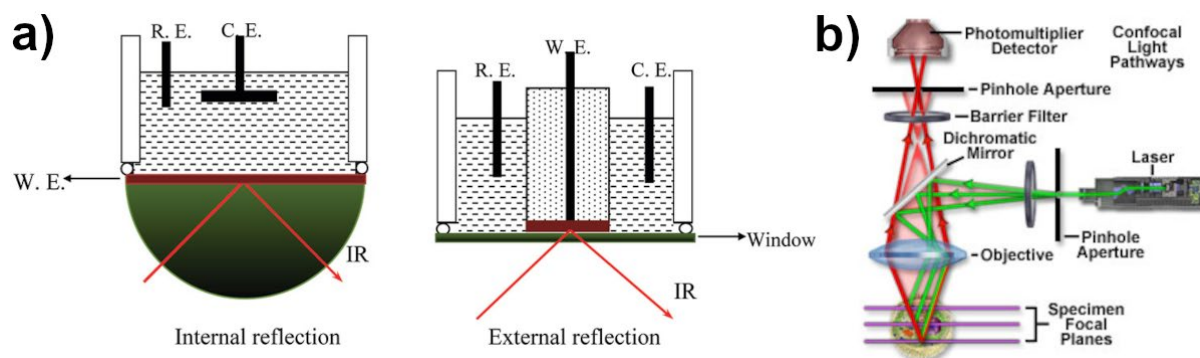


Figure 2. a) Schematic diagrams of in-situ FTIRS cell with internal and external reflection configurations (Reprinted with permission from [33]. Copyright 2012 American Chemical Society); b) Optical configuration of a laser scanning confocal microscope. Reprinted from [34].

In internal reflection configuration, a thin metal film representing the working electrode is deposited on an IR transparent prism with a high refractive index.[35,36] The IR beam is focused on the electrode-electrolyte interface from the back through the ATR prism, and the reflected radiation is then detected without significant absorption from the electrolyte solution. This gives the possibility of working with a higher amount of electrolyte solution and lowering its interference with the reflected IR signal. Apart from IR, Raman spectroscopy has attracted significant interest recently for the in-situ studies of electrochemical processes at the interfaces of the electrodes, thanks to the tremendous technological advances of the experimental setup and detection abilities.[37] The superior step was the coupling with the confocal microscope, providing the improved spatial and depth resolution and the possibility of Raman mapping of the electrode/electrolyte interface phenomena (Figure 2b). Further advancements, such as the use of surface-enhanced Raman scattering (SERS)[38], tip-enhanced Raman spectroscopy (or AFM-Raman), [39] or the integration of Raman spectrometers with the non-optical microscope, such as SEM, allowed to perform two or more analytical techniques on the same sample region, with an exceptionally high resolution.[40] Raman spectroscopy can give insights not only on the chemical nature of the species involved in the electrochemical processes, but it has been demonstrated to be a valuable tool for probing the crystallinity of the investigated systems. Gabrielli and co-workers reported the use of in situ micro-Raman spectroscopy to get complementary information on the crystallization of CaCO_3 precipitated on various substrates by the electro-chemical method.[41] Certainly, micro-Raman spectroscopy can distinguish the various polymorphs of the CaCO_3 ,[42] even if the carbonate anions have the same configurations in the three different known structures (vaterite, aragonite and calcite), showing different Raman spectra.[41]

Raman spectroelectrochemistry can be used as well in quantitative analysis. In this case, working with a confocal microscope requires using a mapping methodology to cover a wider electrode surface in order to provide a representative averaged Raman spectrum. To solve this drawback, orbital raster scanning can be a solution or a fiber optic with an optimized focal distance enables to increase in the spot size (electrode area measured) in the range of 100-200 square microns. The capability of such a configuration combined with the profit from a SERS effect on electrochemically roughened electrodes was already demonstrated for some pharmaceutical compounds [43], and even single-molecule detection is envisioned.[44] Recently, an advanced technique has been reported, which allows for the extraction of the Raman spectra from a deep layer within a diffusely scattering sample. This technique, called spatially offset Raman spectroscopy (SORS), was discovered and reported by Matousek and co-workers. [45] It overcomes the limits of the conventional setup that is restricted to near-surface regions according to the optical limits of the excitation wavelength used. Furthermore, Raman spectroscopy has been successfully used to understand electrochemical processes in various carbon-based nanomaterials. For example, in-situ spectroelectrochemical measurements allowed to follow in real-time the electrochemical reduction of graphene oxide (GO) and doping of graphene.[46,47] The in situ Raman SEC was also applied to other interesting problems, such as tracking the electron transfer between the glassy carbon and chemisorbed nitroazobenzene monolayer [48] or addressing single-or inner tubes in double-wall carbon nanotubes. [49] A recent development concerns an advanced variant of the in situ Raman spectro-electrochemistry, where a micro-droplet electrochemical cell is employed: μ SEC Raman. This approach is convenient for studies on spatially heterogeneous samples, e.g., various nanocarbons and two-dimensional materials. In this experiment, only the part of the sample covered by the micro-droplet is influenced by the applied potential. This technique has been enriched by the implementation of photoluminescence spectroscopy, which enables in situ investigations of excitons in van der Waals materials during electrochemical doping.[50] For a schematic representation, please refer to Figure 3.

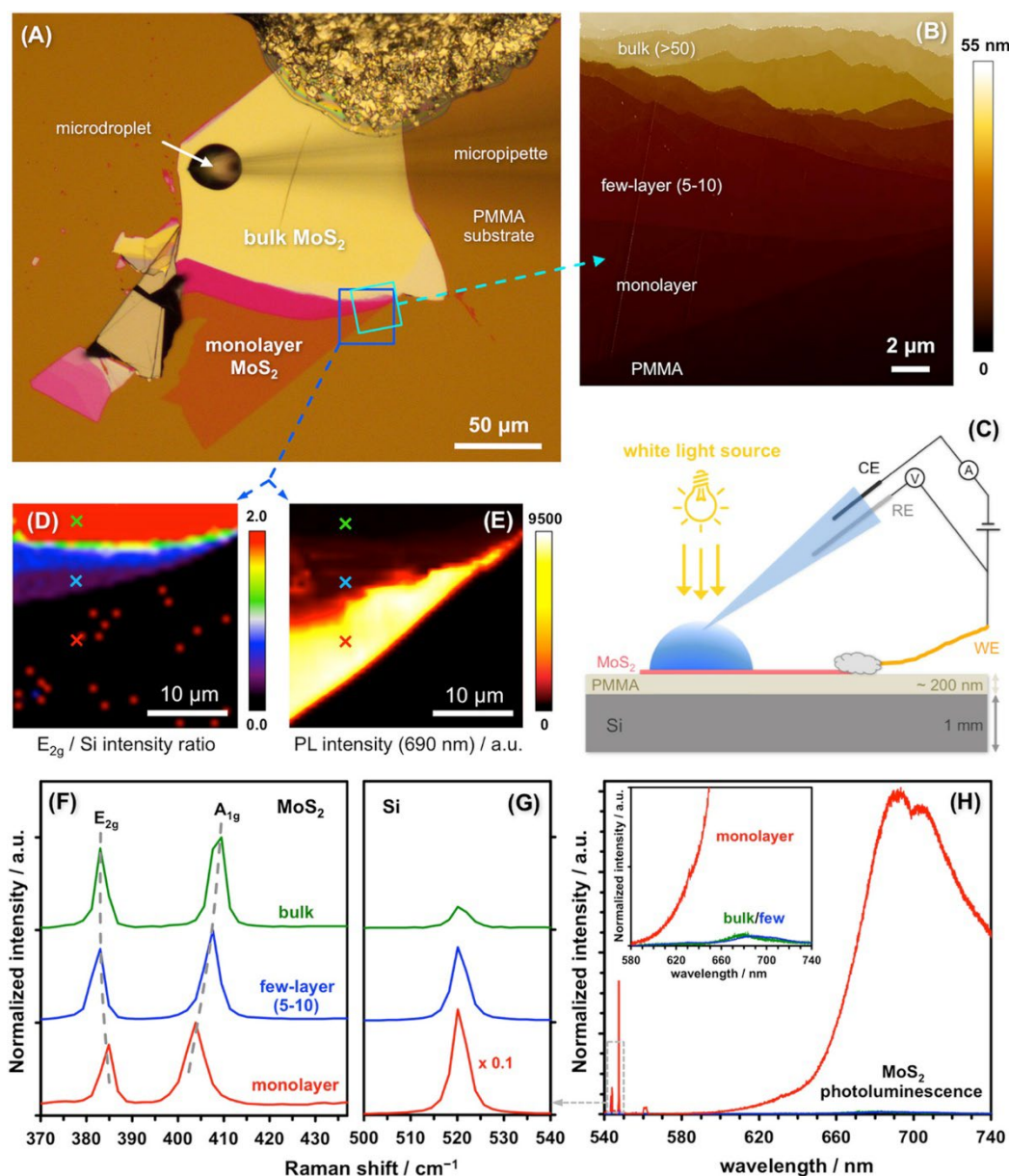


Figure 3. Photo and Raman electrochemical measurement of MoS₂ layers. (A) Optical micrograph of and MoS₂ flake on PMMA-coated Si substrate. (B) AFM micrograph of a selected monolayer/few-layer/bulk flake region. (C) Schematic of the photoelectrochemical setup. (D) Raman map of the E_{2g}/Si intensity ratio. (E) PL intensity map at 690 nm wavelength. (F) and (G) Raman spectra showing the two main MoS₂ bands and the Si band, respectively, and their evolution with the number of MoS₂ layers. (H) PL spectra of the monolayer/few-layer/bulk MoS₂. The areas used for the AFM measurement (B) and the Raman (D) and PL (E) maps are indicated in (A) by light blue and dark blue squares, respectively. The Raman and PL spectra of (F–H) were recorded at spots indicated by colored crosses in (D, E), respectively. (Reprinted with permission from [50]. Copyright 2016 American Chemical Society.)

Besides the vibrational spectroscopies, electronic spectroscopy is also considered for the studies of electrochemical processes at the electrode interface, using the classical UV–vis–near IR

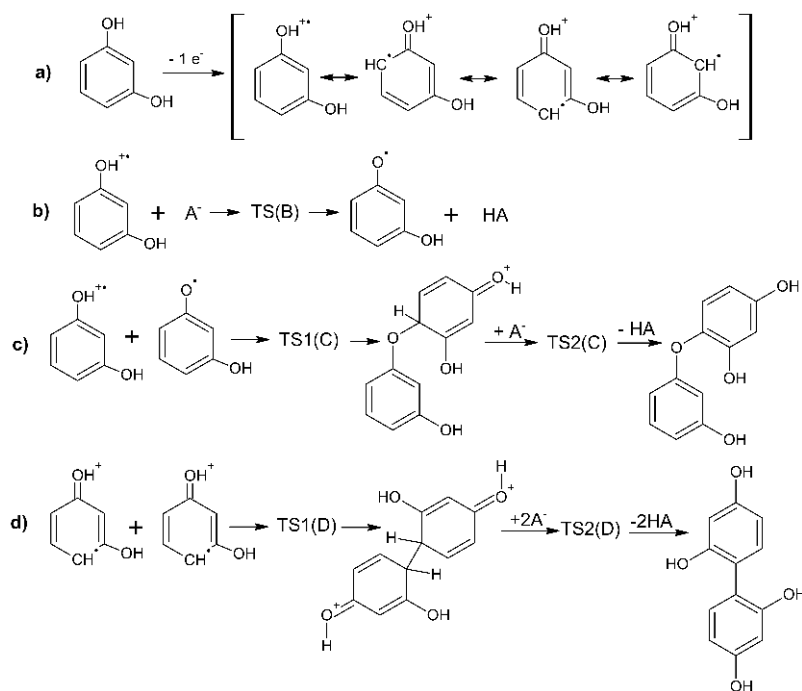
(NIR) absorption as the most applied method in spectroelectrochemistry.[51] The electrochemical processes naturally involve charge transfer reactions, which induce changes in the electronic structure of the molecules, and the UV-Vis-NIR spectroscopy can be applied both in reflection and in transmission configuration in the photon energy range from NIR through visible to the UV region.[51] The introduction of optically transparent electrodes, made of a transparent material (glass, quartz) covered with a thin noble metal film (Pt, Au), Sn and In oxides or using mini-grid electrodes as wire mesh, removed the experimental barrier for the application of UV-Vis-NIR spectroscopy for the study of electrochemical processes in absorption configuration.[52]

[Apart the aforementioned experimental methods, some other less common spectroscopic techniques coupled with electrochemistry *in situ* have been reported such as NMR/EPR\[53\] or Terahertz absorption.\[54\] In particular EPR has been reported to be very sensitive in the study of oxidation/reduction processes in situ probing the intermediately produced spin states and radicals via their g-factors and/or line splitting to get the structural information of the chemical species formed at the electrode. A future perspective is the develop of Terahertz spectroscopy which has been is broadly used for the study of a wide range of functional materials and biological molecules. In fact, the real limitation for such technique is the lack of transparent electrochemical cell for the THz region which span from 0.1 to 10 THz \(3.33–333 cm⁻¹\). Very recently Nemes and coworkers\[54\] reported a THz-transparent three-electrode electrochemical cell for the study of SnO₂ thin films. This approach can open new opportunities in the field of spectroelectrochemistry.](#)

4) Theoretical calculations

The use of theoretical “tools” in electrochemistry spans a variety of different aspects, from numerical simulation of experimental current/potential/time curves to the calculation of electrochemical quantities relying on quantum-mechanical based calculations.[51] The latter results, quite often, concern steady-state properties: in-primis the calculation of HOMO(LUMO) vs. oxidation(reduction) potentials in strictly structurally-related compounds, or quite recently the analysis of standard potentials. The reliability of this approach improved dramatically in recent times thanks to the dramatic increase in computational power due to the unbelievable increase in performance of computers. This grants a great accuracy in calculated electronic structure properties, allowing to tackle also sizable and complex molecular systems. Quite often, the calculated quantities referred to steady-state properties, such as standard potentials [22,23,55], charge transfer rate constants [56], and potential energy surfaces (in particular in

the case of charge and/or radical species – mainly hypothesized as transition state species, usually involved in electrochemical mechanisms). [23] Also, theoretical spectra can be obtained to be compared with the experimental ones [57]. What is more, the real “*atout*” offered by theoretical calculations is the possibility to explore hypotheses that are beyond any possible experimental measurements to validate, for instance, different reaction mechanisms. This can be pursued by exploiting molecular dynamics (MD) calculations, in the case here reported a classical MD trajectory relying on an *ab-initio* potential energy surface. Like, for example, in the polymerization of resorcinol where different reaction paths are probed by, high-accuracy, MD calculations [21]. Another approach, dynamic reaction coordinate (DRC) calculations allowed to pin-point the fundamental role played by the base electrolyte anion in the Kane-McGuire polymerization mechanism, as schematically shown in Scheme 1 (where: the HSO_4^- anion is selected for A^- , for the sake of a suitable comparison with experimental results).



Scheme 1. The scheme shows the single elementary steps considered in the polymerization of resorcinol mainly inspired by following the Kane–Maguire mechanism. [58] (Reprinted with permission from. Copyright 2021 American Chemical Society).

Figure 4 sets out MD data and relevant, interesting molecular geometrical quantities concerning path *c*, compare Scheme 1.

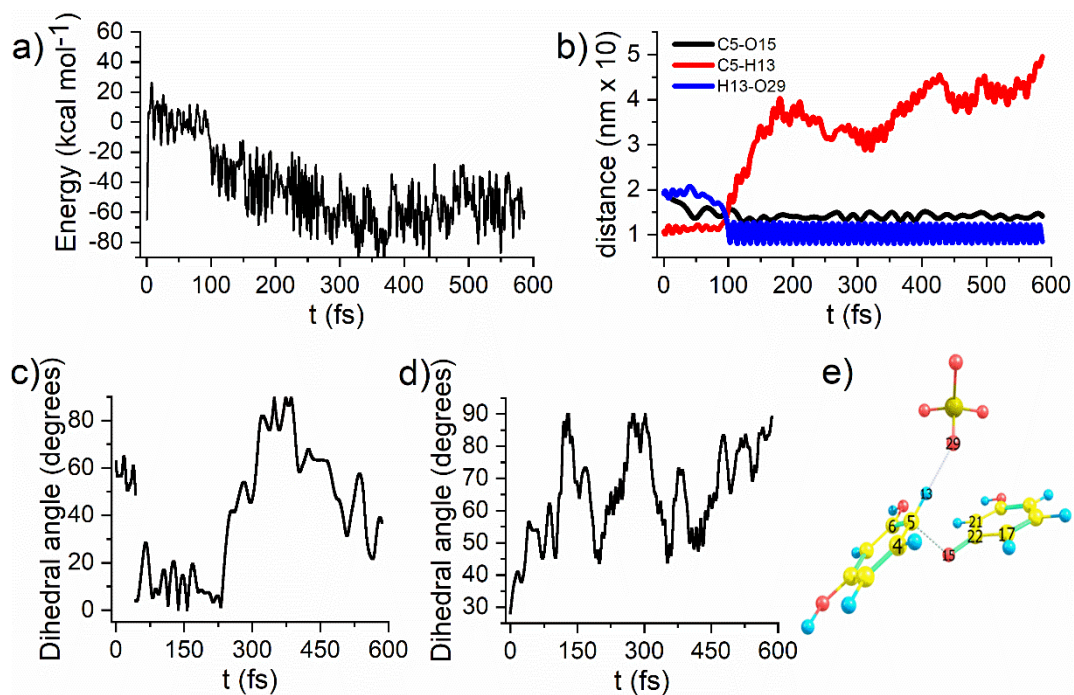


Figure 4. Path (C) DRC results, B3LYP/6-31G(d). a) molecular electronic potential-energy vs time. b) $H_{13} - O_{29}$, $C_5 - O_{15}$, $C_5 - H_{13}$ bonds distances, c) dihedral angle between rings, d) dihedral angle atoms 6 - 4 - 5 - 13, e) molecular model with the relevant numerical labels (Reprinted with permission from [21]. Copyright 2021 American Chemical Society).

5) Perspectives

Molecular electrochemistry evolved in time from a situation where molecular electroactive species were present just in the bulk solution to quite complex systems which feature redox systems grafted (chemisorbed via covalent bonds) directly on the working electrode or in the form of molecular crystals acting as working electrodes [2,16]. Thus, it also developed, eventually, dealing with the cross-field area between solid-state electrochemistry and solid-state electronics. [59–61] Here, the big challenge remains the “order” and purity of the molecular layer present on the electrode surface. Because the electrochemical properties are strongly correlated with the homogeneity of the electrode surface layer, the most promising way to reach the coveted homogeneous thin film is the preparation of a self-assembled monolayer (SAM).[31,62–65] As a future perspective, the use of solution shearing techniques, such as blade coating or bar-assisted meniscus shearing (BAMS), [66–68] have been reported to give the possibility to get the thin film with single crystal-like properties and well-oriented crystal domains and surface homogeneity. [68] Eventually, when dealing with the field of molecular electrochemistry, it must be noted that at present, tight integration between the electrochemical measurements with spectroscopic and theoretical tools paves the way to a thorough understanding of both steady-state and dynamical properties of the overall electrochemical process.

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BAMS: a technique for controlled thin films production (quasi-single crystal), which can be easily implemented in the area of electrode functionalization, paving the way to further extend solid-state electrochemistry measurements, and characterization, to the domain of electronics oriented devices.

Highlights

- The field of molecular electrochemistry is tackled by showing how effective is an integrated approach where electrochemical, spectroscopic (mainly UV-Vis and vibrational: specroelectrochemistry SEC) and theoretical data are strictly compared.
- This work covers also aspects in the area at the interface between solid-state molecular electrochemistry and applications in the field of electronics.
- A quite recent in situ Raman spectro-electrochemistry, μ SEC Raman, is briefly surveyed.
- Ab-initio Molecular Dynamics results are shown to yield a unique valuable tool to probe the reaction mechanism at a molecular level, based on both electrochemical and spectroscopic evidences.