



## Versatile and low cost spectroelectrochemical cell for *in situ* study of electrode surfaces



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### ABSTRACT

We describe here a new low cost spectroelectrochemical cell (SEC), particularly suited to perform confocal reflectance Raman Spectroscopy *in situ* of electrode surfaces taking advantage of surface enhancement effects. The system is readily (dis)assembled, easily adaptable for use with UV-Vis and NIR techniques and allows integration with most commercial devices and operation using different electrodes. Spectroelectrochemical characterization were carried out by using a pre-roughened gold electrode in the presence of 1,4-Bis(Isopropylamino)anthraquinone as an active redox probe. As proof-of-concept, SERS effect of a SSV (Sphere Segment Void) copper substrate was successfully evaluated at different potentials. Raman-assisted electrochemical reduction of graphene oxide was also demonstrated by using our cell, highlighting the applicability and versatility of the proposed SEC.

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## 1. INTRODUCTION

Spectroelectrochemistry is a powerful hybrid technique that enables obtaining electrochemical and spectroscopic information from liquid samples or thin films [1,2]; being especially advantageous in systems where variations in the applied potential can induce changes in the observed spectra. A number of spectroscopic techniques have been coupled to electrochemical systems; an approach that has been proven very powerful and effective [3–7]. In particular, spectroelectrochemical cells (SEC) that enable *in situ* spectral acquisition can be very useful for detection, identification and characterization of short-lived electrochemically-generated species/intermediates, resulting in a detailed investigation of the mechanistic pathways of redox processes [8,9]. However, the combined use of electrochemical and spectroscopic methods involves experimental challenges that need to be addressed properly in order to acquire reliable data. One of the main issues

is to collect spectroscopic and electrochemical data simultaneously keeping in mind differences in temporal responses. Data, appropriately acquired *in situ* on dynamic systems, offer the possibility of closely following redox-induced changes in a system. In comparison, *ex situ* measurements are better suited for samples that are relatively insensitive to changes in experimental conditions.

There are in the literature numerous examples of spectroelectrochemical cells [10–13]. However, in many cases, the cells are designed to operate under quite specific conditions [11,13–15] or for specific equipment [16]. For the specific case of *in-situ* spectroelectrochemistry, by reflectance, of modified surfaces, cell designs are limited and/or of complex design [10,16,17].

Herein we describe a low cost, multi-purpose SEC that can easily operate jointly with most commercial spectrometers and potentiostats for reflectance measurements of modified electrode surfaces. The main novelty in this work is the design that we created to easily fit some of the most common commercially available working electrodes. This characteristic provides great advantage over other SECs when it comes to versatility and ease assembly. In addition, the working electrode in this case is not limited for spectroelectrochemical purposes, being easily detached from the SEC and used normally for electrochemical analysis and to perform specific modifications before the spectroelectrochemical measurements, for instance. Details about the design and

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construction of the cell are provided, as well as representative results obtained with it as a proof-of-concept. Additional information and examples of different setups using the SEC were also presented.

## 2. EXPERIMENTAL SECTION

### 2.1. Practical considerations of the proposed design

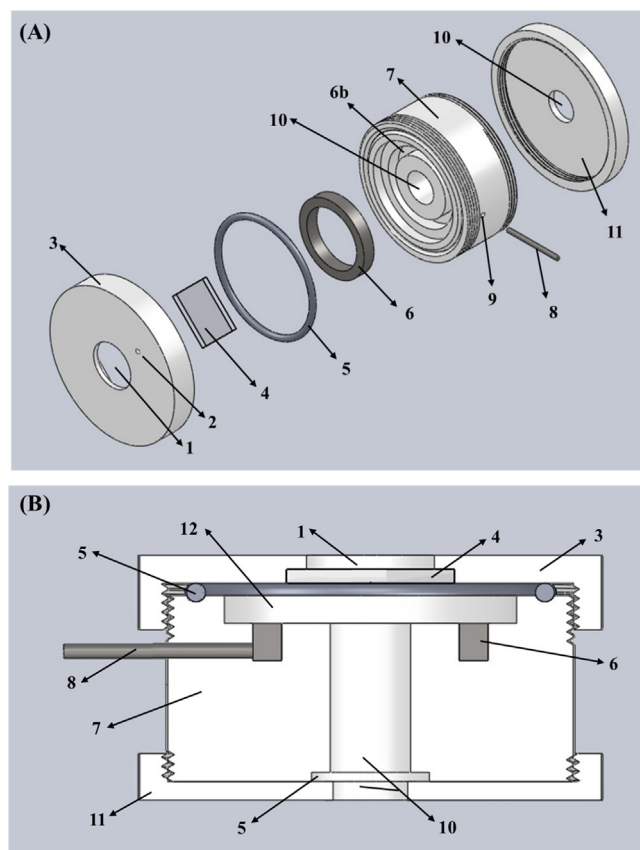
To be broadly employed, a SEC must be practical, adaptable and, preferably, inexpensive. To achieve these objectives, the SEC must be made of low cost, chemically stable and durable materials, with the construction process easy to reproduce and, finally, easily adaptable to the user's needs. We present herein, a fully functional system, compatible with a wide range of spectroscopic and electrochemical equipment including handheld systems, using waveguide probes. The cell is particularly useful in several situations, with two great highlights. First, in situations that require a previous preparation of a modified electrode, such as film deposition or specific surface pretreatment. In these cases, after modifying for conventional electrochemical studies, the electrode can be subsequently mounted into the SEC. This fact overcomes the need of preparing the surface of dedicated electrodes only for spectroelectrochemical measurements like in the commercial ones, therefore, facilitating the correlation and the preparation of the electrode for different analysis. Another advantage of the proposed SEC is in situations that require an electrochemical cell to operate upside down (in relation to the working electrode), with modified electrodes or with limited sample size. Details about the cell body, lid, electrodes and general construction are discussed below.

### 2.2. Cell Body

The cell body was made from poly-ether-ether-ketone (PEEK), a widely available polymer with very high chemical and mechanical resistance. Its high chemical inertness allows the SEC to be used with a wide range of aqueous and non-aqueous solvents, electrolytes and samples. PEEK is also mechanically robust, and easily machinable, especially when compared to poly-tetra-fluoro-ethylene (PTFE) and other chemically resistant polymers. These characteristics can mitigate sealing problems, preventing leaks. PEEK is also opaque, which precludes scattered light from accessing the sample cavity, reducing degradation of photosensitive samples. A detailed image of the SEC is presented in Fig. 1A and B, where it is possible to see the assembled cell and how the various parts are integrated. All cell components are identified and listed in the Figure caption.

Some parameters of the proposed SEC may be adjusted according to the user needs, such as the working electrode (WE) diameter and the inner chamber volume, for instance. The thickness of the liquid layer between the WE surface and the internal side of the quartz window is a key parameter that can influence the quality of data obtained, affecting both spectroscopic signal intensity (a thinner layer makes it easier to focus the laser on the surface) and the availability of electroactive species.

The present SEC design allows controlling the WE distance to the quartz slide by manual adjustment in the axis perpendicular to the lid plane, without compromising the cell seal. The prototype developed and described in this work uses a WE with an outer diameter of 1 cm, which connects tightly to the chamber, but allows sufficient mobility to adjust its position and, consequently, the liquid layer thickness covering it. For the chamber, the dimensions (#12 in Fig. 1B) were 16 mm radius, 3 mm depth and a total volume of 2.4 ml. The volume of electrolyte was determined so as to minimize sample demands, using a thin layer of electrolyte



**Fig. 1.** (A) and (B) Schematic drawings of the spectroelectrochemical cell identifying components and how they are assembled. Listed: 1-Aperture for incident laser; 2-Aperture for reference electrode; 3-Threaded lid; 4-Quartz/glass window; 5-O-ring; 6-Counter-electrode (CE) ring, which fits in the bas relief (6b); 7-Cell body; 8-External connection to the CE; 9-Aperture for (8); 10-Aperture for working electrode (WE); 11-Threaded bottom support/WE seal; 12-Cell chamber.

over the WE to minimize interference from scattered light, keeping just enough sample for carrying the measurements. It is worth noting that there are significant sources of interference to the spectroscopic signal during *in situ* spectroelectrochemical measurements. For instance, the solvent and the chemical species in solution can exhibit intense Raman scattering over the spectroscopic range of interest, thus contributing significantly to light/background scattering. The longer the distance the laser light has to travel through the solution (i.e. path length), the more light will be scattered resulting in a degradation of the signal to noise ratio ( $s/n$ ). These issues highlight the importance of a system that allows operation with thin liquid layers (below 1 mm), thus minimizing detrimental effects, yielding a better signal to noise ratio and shorter data acquisition times. The cylindrical shape was chosen for practical reasons, since it makes the cell easier to machine/fabricate. The absence of sharp corners mitigates bubble formation/trapping inside the chamber, especially during the filling process, which may influence the measurements. Moreover, a rounded shape makes cleaning and maintenance easier.

### 2.3. Cell lid

The lid is a key component of the SEC since it has a transparent window aperture, for the laser to reach the electrode/solution, and is where the reference electrode (RE) is connected. The position and shape of these openings are crucial for an efficient operation,

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