



Simplifying the assessment of parameters of electron-transfer reactions by using easy-to-use thin-layer spectroelectrochemistry devices



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ABSTRACT

UV–Vis absorption thin-layer spectroelectrochemistry greatly contributes to the assessment of parameters of electron-transfer reactions by providing electrochemical and spectroscopic information obtained simultaneously in a confined space around the working electrode. In this work we present an ingenious modification of a spectroelectrochemistry device based on carbon nanotubes and bare optical fibers to perform UV–Vis absorption thin-layer spectroelectrochemistry measurements. The working and counter electrodes are made of carbon nanotubes filtered and press-transferred onto a flat support where a painted silver line acts as pseudo-reference electrode. To perform high sensitivity measurements, two bare optical fibers are fixed to the support in a parallel arrangement. In a novel development, a quartz plate is placed on top of the bare optical fibers in order to create a thin layer whose thickness is reproducibly controlled by the diameter of the optical fibers. This methodology is also successfully applied using commercial screen-printed electrodes. Three different electroactive compounds, ferrocenemethanol, *o*-tolidine and $[\text{Ru}(\text{bpy})_3]^{2+}$, are studied and good results are obtained. As demonstrated below, these long optical path UV–Vis absorption thin-layer spectroelectrochemistry cells considerably reduce the complexity associated with this type of devices, eliminating one of the major disadvantages of this technique and making it much more accessible to the scientific community.

1. Introduction

One of the main aims of chemistry is the development of new compounds with outstanding properties. A thorough characterization of these substances is clearly necessary before their use. As far as electrochemical properties are concerned, spectroelectrochemistry (SEC) techniques [1], particularly thin-layer SEC, can significantly help in assessing a number of parameters for compounds that undergo electron-transfer reactions [2].

UV–Vis absorption thin-layer SEC is a powerful hybrid technique that allows the researcher to simultaneously obtain electrochemical and spectroscopic responses of a chemical system in the few micrometers of the confined solution adjacent to the surface of the working electrode (WE) [3–5]. When the light beam travels in a perpendicular direction with respect to the WE surface in normal configuration [6,7], it collects information about the solution and the WE. However, when the light beam is parallel to the WE, in what is called a parallel arrangement [8], only the solution is sampled. As can be expected, bidimensional thin-layer SEC, the simultaneous performance of normal and parallel SEC,

combines the best features of both arrangements [9]. The advantages provided by UV–Vis absorption thin-layer SEC have been exploited in multiple research fields, including side-reactions [2,10], self-assembled monolayers [11], compounds of biological interest [12–16], photo-voltaic cells [17], optoelectronics [18], conducting polymers [19,20], corrosion phenomena [21], porphyrins [22] and metal complexes [23–27].

The use of carbon materials in electrochemistry is increasing rapidly [28–30]. For instance, the growing importance of carbon nanotubes (CNTs) is explained by the remarkable properties that this carbon allotrope possesses [31–33]. In a previous work, we developed a methodology based on filtering a dispersion of CNTs [34] that enables us to transfer homogeneous CNT films onto different supports [34–37]. These CNT electrodes have demonstrated excellent performance as optically transparent electrodes [34,36] and for the quantitative determination of analytes [35,37].

Several devices, some of which are cited in this contribution, have been widely used and have laid the groundwork for numerous UV–Vis absorption thin-layer SEC research studies. Nevertheless, it should be

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noted that the complexity of the existing UV–Vis absorption thin-layer SEC cells is one of their most important drawbacks. On the one hand, the normal transmission arrangement needs optically transparent electrodes, drastically reducing the number of electrodes that can be used. On the other hand, a perfect but difficult alignment of the light beams is required in the parallel configuration. In practice, this means that many different parts must be duly assembled to carry out a single experiment. To overcome these problems, we are going to focus on two areas that, in recent years, have attracted great interest in this research field: (i) the use of CNT networks [38,39] and (ii) the use of optical fibers in long optical path cells whose origin, curiously, can actually date back to the early 1980s [40].

In this paper we develop an easy-to-use device to perform UV–Vis absorption thin-layer SEC experiments in a friendly way, based on CNT electrodes and bare optical fibers set up in a parallel configuration, allowing us to work with both transparent and non-transparent WEs. The thickness of the thin layer is solely controlled by three bare optical fibers with a quartz plate laid on top of them. The distance between the two optical fibers carrying light determines the length of the optical path, allowing us to study electroactive compounds with very different molar absorption coefficients with high sensitivity. The third optical fiber is only used as a spacer. Although the main focus of this work is on the use of CNTs as electrode material, our methodology has also been applied to commercial carbon screen-printed electrodes (SPEs). The cells have been tested with ferrocenemethanol (FcMeOH), *o*-tolidine, and $[\text{Ru}(\text{bpy})_3]^{2+}$ and the main electrochemical parameters of their electrochemical reactions (formal potential and electrons transferred) have been determined.

2. Experimental

2.1. Reagents and materials

Single-walled carbon nanotubes (SWCNTs, Sigma-Aldrich), 1,2-dichloroethane (DCE, 99.8%, for HPLC, Acros Organics), polytetrafluoroethylene membranes (filter pore size 0.1 μm , JWVP01300, Millipore Omnipore), polyethylene terephthalate (PET, 175 μm thick, HiFi Industrial Film), silver conductive paint (Electrolube) and transparent nail polish (Essence) were used to fabricate the electrodes based on CNTs. Carbon SPEs (DRP-110, DropSens) were used as commercial electrodes. Three bare optical fibers (100 μm in diameter, Ocean Optics) and a quartz plate (Sugelabor) were required to develop the UV–Vis absorption thin-layer SEC devices. FcMeOH (97%, Acros Organics), *o*-tolidine (Aldrich Chemical Company, Inc.), $[\text{Ru}(\text{bpy})_3]^{2+}$ (Tris(2,2'-bipyridyl)ruthenium(II) chloride, hexahydrate, 98%, Acros Organics), KCl (Acros Organics), acetic acid (VWR) and HClO_4 (60%, Panreac) were used to prepare the solutions. All reagents were used as received without further purification. All chemicals were of analytical grade. Aqueous solutions were freshly prepared using ultrapure water (18.2 $\text{M}\Omega\text{ cm}$ resistivity at 25 $^\circ\text{C}$, Milli-Q Direct 8, Millipore). All handling and processing were performed carefully, particularly when DCE was used.

2.2. Instrumentation

The SEC set-up included a potentiostat/galvanostat (PGSTAT302N, Metrohm Autolab), a halogen–deuterium light source (AvaLight-DH-S-BAL, Avantes) and a spectrometer (QE65000, 198–1006 nm, Ocean Optics). Stencils were made of poly(methyl methacrylate) (Maniplastic) using a CO_2 laser cutting machine. A tip-sonicator (CY-500, Optic ivymen System) and a laboratory hydraulic press (SpectroPress, Chempex Industries, Inc.) were also used in this work.

2.3. Fabrication of the long optical pathway UV–Vis absorption thin-layer SEC devices

The development of the present cells is based on a previous design of our group devised to carry out quantitative SEC analysis in a semi-infinite diffusion regime [37], which has been ingeniously adapted to develop the thin-layer SEC devices presented in the current work. Briefly, 2 mL of a sonicated SWCNT dispersion were filtered and the homogeneous SWCNT film deposited on the membrane was press-transferred onto a PET support using a stencil with the desired shape. This methodology, which allows us to fabricate a three-electrode cell with a WE and a counter electrode (CE) of SWCNTs and a Ag pseudo-reference electrode (RE) made with silver conductive paint, is optimal as the three electrodes are completely flat on the support, without the typically large RE and CE. Electrical contacts were made with silver conductive paint and were electrically isolated using nail polish. Afterwards, two 100 μm bare optical fibers were aligned opposite one another and fixed to the PET support with nail polish, taking care that the bare optical fibers were not covered with this adhesive. A common adhesive tape can also be used for this purpose in the development of this device. The misalignment of optical fibers separated by a gap causes significant losses in the amount of collected light and, consequently, a deterioration of the signal/noise ratio. For this reason, the procedure used to perfectly align the bare optical fibers, with their ends partially touching the WE surface, involved pressing them towards the support and looking for the largest number of photons that arrived at the detector, while the nail polish was drying. When it was totally dry, a drop of only 20 μL of solution was deposited on the WE after homogenization. Subsequently, in order to establish the thin-layer diffusion regime, a quartz plate was simply placed on top of the bare optical fibers, pressing the drop between the support and the quartz plate and covering the three electrodes and the ends of the bare optical fibers with the sample solution. A bare optical fiber (used as a spacer) was also placed before this last step to ensure that the quartz plate was parallel to the PET slide. This makes the assembly extremely easy. Although other materials could be used, the quartz plate was selected due to its relatively high weight, which helps to establish the thin-layer, and to its transparency, which enables us to observe the system. It should be noted that this quartz plate allows us to work in normal and even in bidimensional arrangements. Fig. 1a illustrates this UV–Vis absorption thin-layer SEC device based on CNT electrodes. It can be seen that the bare optical fibers in a parallel configuration with respect to the WE control both the optical path length (distance between the optical fibers) and the thin-layer thickness, which is actually the diameter of the optical fibers (ca. 140 μm due to the cladding material). Finally, one of the bare optical fibers was connected to the light source and the other to the monochromator/detector, and the electrical contacts to the potentiostat.

Although the method for fabricating this device based on CNT electrodes is simple and available to all laboratories, we have also applied our methodology to the use of commercial SPEs. By fixing the bare optical fibers directly to a carbon SPE using nail polish and employing the same quartz plate as before, we can successfully control the thin-layer thickness, greatly increasing the ease of performing the measurements (Fig. 1b). This demonstrates that our cell geometries do not require optically transparent electrodes, making the approach very interesting in terms of the use of opaque materials.

Several advantages of these novel UV–Vis absorption thin-layer SEC cells should be highlighted, including the possibility of using non-transparent electrodes, the increase in sensitivity due to the long optical path length and the excellent time/potential and spectral resolution (see Fig. 1c to follow the spectra evolution recorded during a cyclic voltammetry of $[\text{Ru}(\text{bpy})_3]^{2+}$). The ease of performing UV–Vis absorption thin-layer SEC measurements and the simplicity of controlling both the optical path length and the thickness of the thin layer must be emphasized.

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