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Simultaneous study of different regions of an electrode surface with a novel spectroelectrochemistry platform

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Abstract

A spectroelectrochemistry device capable of studying different regions of an electrode surface in a strictly simultaneous way is presented in this work. It is based on two reflection probes placed in near-normal arrangement with respect to an electrode surface partially modified on purpose. As expected, the electrochemical signal contains information related to the whole system, being impossible to distinguish which behaviour corresponds to the unmodified and which one to the modified part of the electrode. Spectroelectrochemistry provides an excellent solution because the reflection probes fully explain the electrochemical response, allowing us to deconvolve the electrochemical behaviour from an optical point of view under exactly the same experimental conditions. To demonstrate the usefulness of this platform, a highly oriented pyrolytic graphite electrode is partially modified with carbon nanotubes or graphene, all of them commercially available, and the dopamine oxidation at the different parts of the electrode is simultaneously studied. A remarkable decrease of the onset oxidation potential is observed at the modified surfaces with respect to the bare electrode. This work increases the advantages of spectroelectrochemistry for the characterization of materials and the comparison of electrode surfaces, laying the groundwork for novel experiments in which the simultaneity is a key factor.

Keywords

Spectroelectrochemistry; reflection probe; carbon nanotubes; graphene; dopamine; in situ technique.

1. Introduction

In general, the course of an electrochemical reaction is strongly dependent on the electrode properties. For this reason, multiple research studies are focused on the modification and characterization of electrode surfaces to improve their properties [1–4]. Among all the existing techniques, those based on electrochemistry are widely used, being scanning electrochemical microscopy (SECM) [5–7] and scanning electrochemical cell microscopy (SECCM) [8–10], for example, some of the most important ones due to their excellent features.

The possibilities offered by in-situ and real-time multi-response techniques are well known. It should be highlighted the importance of spectroelectrochemistry [11,12], a technique that contains the optical information related to an electrochemical experiment. This hybrid technique possesses a great specificity and offers a complete understanding of an electron-transfer process not only from an electrochemical but also from a spectroscopic point of view [13–20], being the simultaneity one of its most significant advantages. As is known, simultaneity plays a key role in a broad range of measurements to reduce costs and experimental time, and, what is more important, to be certain about the properties of a system.

Therefore, the main objective of this work is to develop a UV-Vis absorption spectroelectrochemistry platform for a strictly simultaneous comparison of different parts (unmodified and modified) of an electrode surface. For the modification, carbon nanotubes and different types of graphene are used according to their remarkable properties and sensing applications [21–29]. Thus, in a single experiment, using the same solution drop and under exactly the same experimental conditions, we are able to obtain two spectroscopic responses, one for the unmodified and one for the modified part of the electrode, that together explain the electrochemical signal associated with the whole electrode in a comprehensive way. Our spectroelectrochemistry tool presents specific advantages with respect to, i.e, a multichannel potentiostat, such as the obtaining of optical information concomitantly with the electrochemical signal and the use of a single heterogeneous (partially modified) working electrode (WE) instead of different WEs. In this communication we show one of the most interesting applications of this ingenious spectroelectrochemistry setup but there are a lot of possibilities in the field of characterization of materials and modification of electrodes, among others.

2. Experimental

2.1. Reagents and materials

Highly oriented pyrolytic graphite (HOPG, 15 x 15 mm, GoodFellow), single-walled carbon nanotubes (SWCNTs, 0.7-1.1 nm in diameter, (7,6) chirality, Sigma-Aldrich), graphenes (G40, av-40-1-2,5, Avanzare Innovación Tecnológica; G70, av-70-1-2,5 Avanzare Innovación Tecnológica), 1,2-dichloroethane (DCE, 99.8%, for HPLC, Acros Organics), nitrocellulose membranes (filter pore size 0.45 µm, HAWP01300, Merck Millipore), adhesive tape, polyethylene terephthalate (PET, 175 µm thick, HiFi Industrial Film), poly(methyl methacrylate) (PMMA, Maniplastic), aluminium foil, silver conductive paint (Electrolube), Kapton and transparent nail polish (Essence) were used to fabricate the electrodes. Ferrocenemethanol (FcMeOH, 97%, Acros Organics), dopamine (DA, dopamine hydrochloride, 99%, Acros Organics), KCl (Acros Organics) and $HClO_4$ (60%, Panreac) were used to prepare the solutions.

All chemicals were of analytical grade and used as received. Aqueous solutions were freshly prepared using ultrapure water (Milli-Q Direct 8, Millipore). All handling and processing were performed carefully, particularly when DCE was used.

2.2. Instrumentation

Setup included a potentiostat/galvanostat (PGSTAT302N, Metrohm Autolab), a halogen-deuterium light source (AvaLight-DH-S-BAL, Avantes), a bifurcated optical fiber (Ocean Optics), two optical fiber reflection probes (2.5 mm in diameter, Avantes) and two spectrometers (QE65000, Ocean Optics). A tip-sonicator (CY-500, Optic ivymen System) was also used to prepare the carbon nanomaterial dispersions.

2.3. Fabrication of the electrodes and the spectroelectrochemistry platform

The electrodes were fabricated with HOPG employing an adhesive tape. For their modification, each commercial carbon nanomaterial was dispersed applying different sonication levels in increasing volumes of DCE, obtaining dispersions of 0.5 mg in 100 mL. Before using them, 10 mL of the dispersions were sonicated to ensure a good homogeneity. A low-pressure methodology based on one of our previous works [30] was used to transfer a film of the nanomaterial on a part of the HOPG electrode in order to modify the surface. Briefly, 1 mL of the dispersion was filtered under vacuum through the nitrocellulose membrane and, without letting dry, the carbon nanomaterial film formed on the membrane was transferred to a part of the HOPG electrode applying a slight finger pressure using a PET sheet and a PMMA piece. Thus, HOPG electrodes partially modified with SWCNTs, graphene G40 or graphene G70 were obtained. Silver conductive paint, employed to make the electrical contact to the aluminium foil, was dried at room-temperature. A Kapton mask with two equal holes (2.5 mm in diameter) was placed to control the area of both unmodified and modified regions of the electrode. Finally, nail polish was used to isolate the electrical contact from the solution and a PET sheet was placed under the electrode to improve the planarity of the system. Using this methodology, HOPG electrodes without modification and HOPG electrodes partially modified with SWCNTs (HOPG-SWCNTs) or with different kinds of graphene (HOPG-G40 and HOPG-G70) have been fabricated.

The spectroelectrochemistry platform was fabricated using a CO_2 laser cutting machine. For the sake of clarity, a schematic illustration (not to scale) is displayed in Fig. 1a. It consists of a PMMA structure with two identical holes of 2.5 mm in diameter (whose centres are separated by 6 mm that is the spatial resolution) to place two reflection probes (2.5 mm in diameter) for obtaining the optical signals. Their position with respect to the WE surface is exactly the same and each of them is used to study one of the regions of the electrode. The gap from the two parts of the heterogeneous WE to reflection probes is ca. 2.6 mm. In addition, the cell has two holes to place a homemade Ag/AgCl/KCl 3 M reference electrode (RE) and a platinum wire counter electrode (CE) in a middle position with respect to the unmodified and the modified electrode surfaces. The WE is just placed under the reflection probes, guaranteeing the versatility of the surfaces that can be studied and the ease of use of this spectroelectrochemistry platform. The electrodes are connected to the potentiostat and the reflection probes are both connected to the deuterium light source and each of them to a different spectrometer. A sample volume of only 400 µL is required and the integration time for the spectrometers is in the range of 50-300 ms. The initial solution is taken as reference spectrum. In this way, while the electrochemical signal contains the information related to both unmodified and modified parts of the electrode, the spectroscopic data concomitantly taken with the electrochemical response are able to distinguish the behaviour of the analyte with respect to each surface, all strictly at the same time.

3. Results and discussion

Firstly, a HOPG electrode without modification is used with a typical probe such as FcMeOH for the validation of the system [30]. Spectroelectrochemistry experiments were performed using voltammetry of $5{\cdot}10^{-4}$ M FcMeOH in 0.1 M KCl between -0.20 V and +0.60 V at 0.010 $V{\cdot}s^{-1}$. As expected, the voltammogram shows only one behaviour corresponding to the anodic peak associated with FcMeOH oxidation (Fig. 1b). In the same way, the derivative voltabsorptograms at 282 nm at two parts of the HOPG electrode are identical (Fig. 1c). It can be observed the excellent agreement between the peak potentials obtained with the electrochemical (Fig. 1b) and the optical (Fig. 1c) responses. Therefore, the same information was obtained at any part of the electrode surface because a HOPG electrode without modification was used, indicating the good performance of the spectroelectrochemistry platform.

To demonstrate the exciting possibilities of this device, HOPG-SWCNTs, HOPG-G40 and HOPG-G70 electrodes were studied, corresponding to the HOPG electrodes partially modified with the commercial nanomaterials. DA was chosen as target molecule according to the importance of this neurotransmitter whose analysis by electrochemical methods often includes an electrode modification to obtain good figures of merit [31–33]. The behaviour of DA on a HOPG-G70 electrode using a solution $5{\cdot}10^{-3}$ M DA in 1 M $HClO_4$ and applying a voltammetry between 0.00 V and +1.00 V at 0.010 $V{\cdot}s^{-1}$ is plotted in Fig. 2. As can be seen in Fig. 2a, the voltammogram shows two different behaviours. The presence of two anodic peaks is due to the two different types of electrode surfaces present on the WE. This electrochemical signal is rather poor because it cannot explain, for example, (i) which behaviour corresponds to each surface or (ii) the onset oxidation potential at which the electrochemical process corresponding to the second anodic peak begins.

To obtain this valuable information, the optical responses obtained in both regions of the electrode simultaneously with the electrochemical signal are definitely required. Fig.

2b and Fig. 2c show the spectra evolution with potential recorded during the voltammetry at the bare HOPG surface and at the HOPG region modified with G70, respectively. As can be seen, the oxidation of DA at the unmodified HOPG surface starts at an onset oxidation potential higher than at the HOPG surface modified with G70. Therefore, thanks to spectroscopy, we are able to associate the oxidation of DA at the bare HOPG surface with the second peak of the voltammogram and to relate the oxidation of DA at the HOPG surface modified with G70 to the first peak of the voltammogram.

In addition, enlarged views of the corresponding voltabsorptograms in the potential window of interest and at a wavelength of 391 nm [34–36] are displayed in the insets of Fig. 2b and Fig. 2c. These voltabsorptograms indicate that the onset potential of the electrooxidation of DA is +0.671 V at the unmodified HOPG surface while it decreases to a lower value, +0.522 V, for the HOPG surface modified with G70. The criterion assumed to define and determine the onset oxidation potentials from the experimental absorbance at 391 nm is indicated in Table 1. It is important to emphasise that all this information is obtained in a strictly simultaneous way.

In order to observe this behaviour using other carbon nanomaterials, HOPG was also partially modified with G40 or SWCNTs (HOPG-G40 or HOPG-SWCNTs). Although the overlap between the anodic peaks is not always the same, even for the same kind of electrodes, the spectroscopic results (shown in Table 1) demonstrate good reproducibility and indicate that these commercial carbon nanomaterials are capable of reducing the onset oxidation potential of DA in a similar way with respect to the bare HOPG surface.

4. Conclusions and future work

Electrochemistry alone is sometimes unable to provide enough information about the behaviour of an electrode surface. Therefore, a novel spectroelectrochemistry platform is herein presented. As proof of concept, the surface of a HOPG electrode is partially modified with different commercial carbon nanomaterials to compare the behaviour of DA on both surfaces. While the electrochemical signal is related to the whole electrode, each spectroscopic response extracts simultaneous information exclusively associated with the electrochemical process occurring in the electrode region sampled by its reflection probe, separately. The onset oxidation potential of DA in the modified regions with carbon nanotubes or graphene is decreased with respect to the bare HOPG surface. It should be noted that only one solution drop and a single WE are used in a strictly simultaneous way under exactly the same conditions.

This device offers a new way to do spectroelectrochemistry, allowing researchers to study different regions of a surface with a large number of possibilities to compare different electrocatalysts and to understand the reaction processes that take place. Simultaneity is especially crucial in systems that evolve with time. Therefore, as the electrode can be modified with two different materials at the same time, this spectroelectrochemical tool could be of potential interest to compare biological systems, among other applications. Limitations of this platform are mainly technical. The spatial resolution, which depends on different factors, could be improved with (i) a higher number of reflectance probes and spectrometers employed (two in this case), (ii) a lower diameter of the reflectance probes (2.5 mm in this work), (iii) a lower distance between them (6 mm in the present work, which is the current spatial resolution), or (iv) a higher potential scan rate (0.010 $V \cdot s^{-1}$ in the present case) due to diffusion processes. By taking these factors into account, the spatial resolution that could be reached using this technology should be estimated in the order of hundreds of micrometers.

Up to now, the improvement of the properties of an electrode for electroanalysis has usually been studied in consecutive experiments by obtaining the response of the bare electrode and, afterwards, that of the modified electrode. Our work can greatly help to improve this methodology not only by reducing experimental cost but also by comparing diverse surfaces at the same time. The study of the diffusion regimes at the different surfaces [37,38], the comparison of the properties of other materials and the study of more biomolecules and real samples constitute some of the following goals to be achieved.

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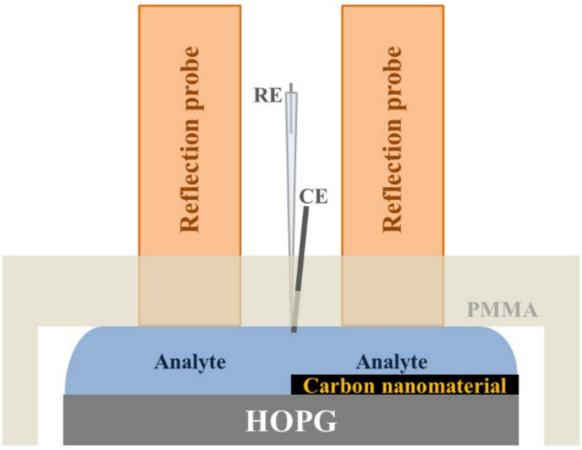

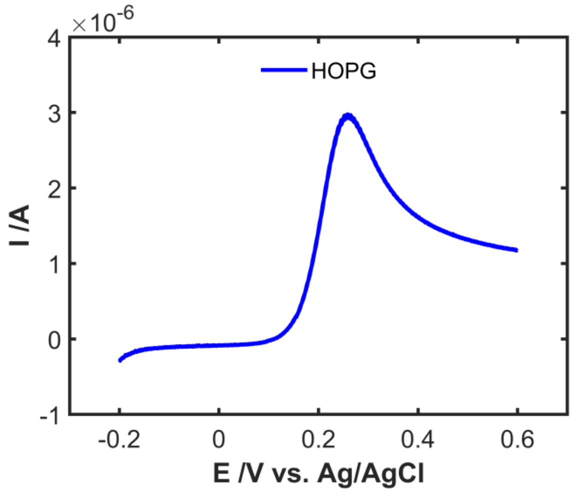

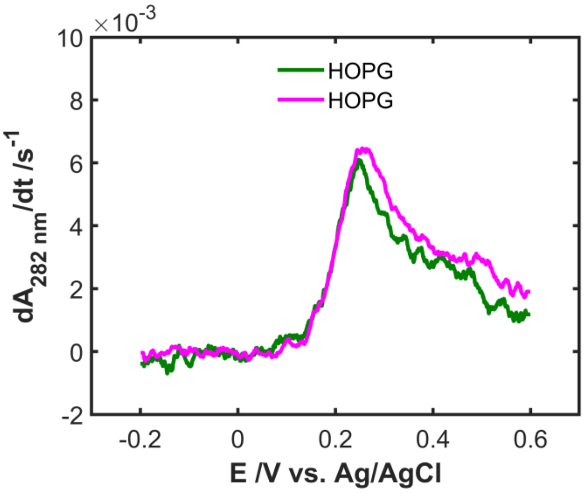

Fig. 1. (a) Illustration of the spectroelectrochemistry platform. (b) Voltammogram and (c) derivative voltabsorptograms at 282 nm at two parts of a HOPG electrode without modification of a spectroelectrochemistry experiment of FcMeOH.

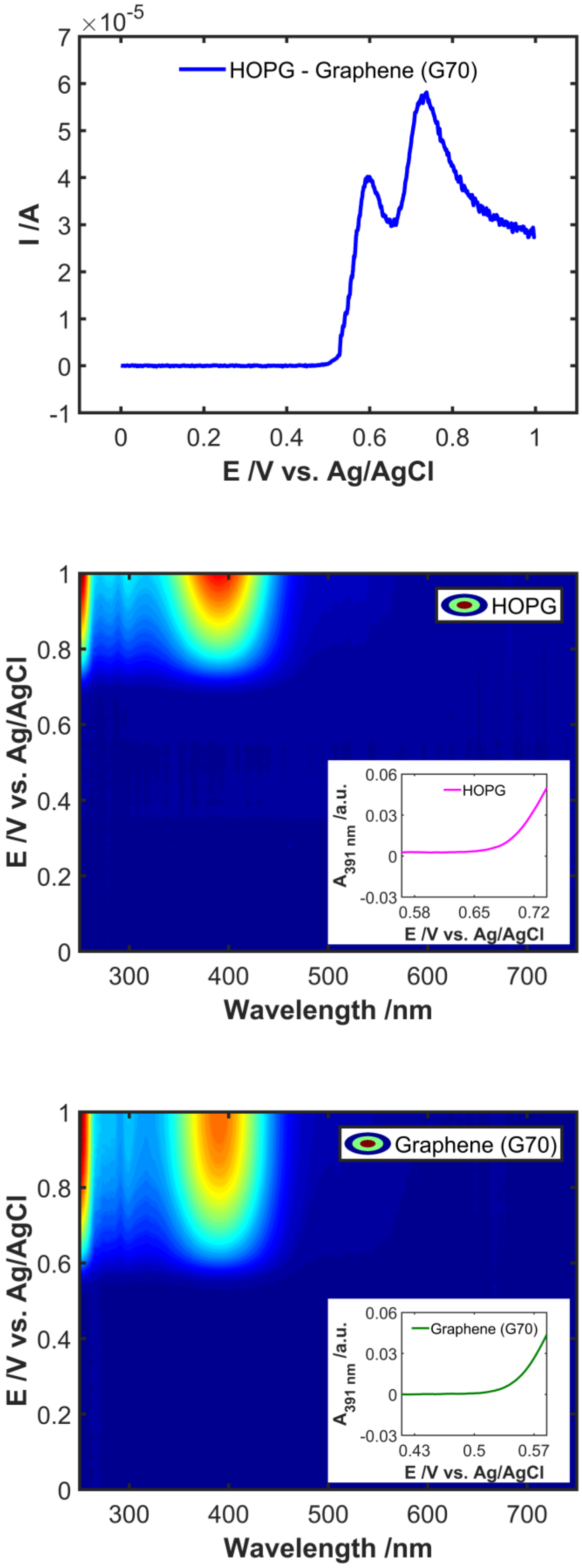

Fig. 2. (a) Voltammogram and spectra evolution with potential (b) for the HOPG part and (c) for the G70 part of a spectroelectrochemistry experiment of DA employing a HOPG-G70 electrode. Insets of (b) and (c) show the enlarged views around the onset oxidation potentials of the corresponding voltabsorptograms at 391 nm.

Table 1. Onset oxidation potentials (in volts, vs. Ag/AgCl) obtained from the spectroscopic signal and using three different electrodes, at which the electrooxidation of DA starts to take place, together with the mean and the relative standard deviation (RSD) values. Onset oxidation potentials, obtained from the experimental absorbance at 391 nm, are the potentials at which the absorbance at 391 nm takes a value corresponding to ten times the standard deviation of the optical signal before the oxidation of DA.

	HOPG-G40		**HOPG-G70**		**HOPG-SWCNTs**	
	HOPG	G40	HOPG	G70	HOPG	SWCNTs
1	0.656	0.539	0.670	0.520	0.642	0.552
2	0.633	0.526	0.661	0.517	0.746	0.531
3	0.616	0.539	0.644	0.506	0.621	0.516
Mean	0.635	0.534	0.658	0.514	0.669	0.533
RSD (%)	3.16	1.40	2.01	1.43	10.00	3.39