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XPS analysis of glassy carbon electrodes chemically modified with 8-hydroxyquinoline-5-sulphonic acid

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Glassy carbon (GC) modified electrodes were obtained by cycling the potential in an 8-hydroxyquinoline-5-sulphonic acid (HQSA) solution. These electrodes were successfully tested as sensors of some species of alimentary and pharmaceutical interest, showing improved performances with respect to those of unmodified GC electrodes and of GC electrodes cycled under the same experimental conditions but in the absence of HQSA. As a matter of fact, in the wide potential range explored for modifying the electrodes, even in the absence of HQSA, complex redox processes leading to the production of several functional groups take place at the surface of glassy carbon itself. An XPS investigation was consequently performed to better understand the effective nature of active species present on the surface of HQSA modified electrodes. The spectroscopic experiments involved acquiring survey and detailed scans of an HQSA powder standard sample and of GC electrodes cycled both in the presence and in the absence of HQSA. The experimental value of the binding energy of the $S2p_{3/2}$ level of HQSA-modified electrodes was found equal to that of the HQSA standard powder, thus confirming that HQSA molecules are adsorbed on the surface of the GC/HQSA electrodes and that they maintain their chemical structure and properties. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: glassy carbon electrodes; 8-hydroxyquinoline-5-sulphonic acid; cyclic voltammetry; XPS; electrode surface functionalities

Introduction

A study is in progress aimed to develop and characterize new modified glassy carbon (GC) electrodes suitable for quantifying species of environmental, alimentary, and pharmacological concern.[1–5] In particular, a modified GC electrode was recently prepared by cycling the potential in 8-hydroxyquinoline-5-sulphonic acid (HQSA) solutions.[4,5] The electrochemical characterization concerned with the optimization of the deposition parameters (HQSA concentration, negative and positive potential limits, number of cycles, nature and pH of the supporting electrolyte). The HQSA modified electrode was evaluated as a sensor of some species of alimentary and pharmaceutical interest (dopamine, methylxanthines, food colorants, ascorbic acid). It can be shown that the above mentioned modification leads to improved electrochemical performances with respect to those of the bare GC electrode and of a GC electrode cycled under the same experimental conditions but in the absence of HQSA.[4,5] This because of the adsorption capabilities made possible through electrostatic attraction and/or ion exchange between the negatively charged sulfonic acid functionality of HQSA and the positively charged groups of the analytes. It is well known, from investigations performed in different support electrolytes,[6–9] that cycling GC electrodes in wide potential ranges such as the one used in our work (Refs. [4,5] and the Experimental section), can also induce complex redox reactions on the GC electrode surface itself, even in the absence of HQSA. These reactions produce electrochemically active surface functional groups such as quinones, quinone-like, phenolic and/or alcoholic groups.[6–9]

Preliminary XPS experiments were then performed in parallel with electrochemical measurements[5] to verify the actual results of the investigated electrode modification. Those experimental findings suggested the convenience of performing a further in-depth XPS investigation to better elucidate the actual surface chemistry of the HQSA modified GC electrodes and, in particular, of allowing a more confident identification of sulphur functional groups on the surface of HQSA-modified electrodes.

This paper describes the results of the XPS characterization of GC electrodes cycled in the presence or in the absence of HQSA (GC/HQSA and GC/ox, respectively) and of an HQSA powder standard.

The results are evaluated and compared in the light of previous literature information.

Experimental

Chemicals

Ultrapure water was obtained by passing house-distilled water through a Simplicity 185 (Millipore S.A., Molsheim, France) water purification system. HQSA (molecular formula $C_9H_7NO_4S$, Sigma-Aldrich, Milan, Italy) and the other reagents were of analytical grade and used as received.

Instrumentation

Electrochemical experiments were performed by a model 1030 multipotentiostat (CH Instruments, Austin, TX, USA) connected

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to a personal computer. The three-electrode cell consisted of modified or bare GC working electrodes (2 mm diameter, Metrohm, Herisau, CH), an Ag/AgCl (KCl 3.0 M) reference electrode, and a Pt counter electrode. All electrochemical experiments were conducted at room temperature ($22 \pm 2\,^{\circ}C$).

The pH of the solutions was measured by a Thermo Orion, Model 420 pH meter (Thermo Fisher Scientific, Inc., Waltham, MA, USA).

X-ray photoelectron spectroscopy spectra were obtained with a ThermoVG Thetaprobe spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a microspot monochromatised AlKα source. The AlKα line (1486.6 eV) was used throughout; the base pressure during acquisition of spectra was $2–3 \cdot 10^{-9}$ mbar. The X-ray beam spot was 400 μm. The energy scale of the spectrometer was calibrated using the $Cu2p_{3/2}$ and Au $4f_{7/2}$ signals at 932.7 and 84.0 eV, respectively. The analysis was performed by acquiring survey scans (binding energy (BE) range 0–1200 eV, FAT mode, pass energy = 150 eV) and detailed spectra of C1s, O1s, Si2p, Cl2p, N1s, and S2p regions (FAT mode, pass energy = 50 eV). Data were analysed using the Avantage software package (Version 3.99 Thermo Fisher Scientific Inc., Waltham, MA, USA), consisting of a nonlinear least-squares fitting program. The experimental points of detailed spectra were fitted using Gaussian–Lorentzian peaks having a full width at half maximum equal to 1.32, 1.45, and 1.33 eV for C1s, N1s, and S2p signals, respectively. The asymmetric graphitic peak in the C1s region was fitted with a full width at half maximum equal to 1.06 eV and using the following tail parameter: tail mix (%) = 55.48, tail height (%) = 0.82, tail exponent = 0.9001. The maximum error on peak positions was + 0.2 eV. Both GC/ox and GC/HQSA electrode exhibited a nearly negligible surface charge. The HQSA powder, being nonconductive, required a more significant calibration of BE values. The sample charging effects were minimized with a low-energy flood gun. In any case, charge referencing of all the experimental BE values was made by setting the binding energy of C1s hydrocarbon photopeak at 285.0 eV. Quantification was made by peak area. The comparison of data from different elements was enabled by correction with empirically derived atomic sensitivity factors (C1s = 1.0, N1s = 1.8, O1s = 2.93, S2p = 2.1, Cl2p = 2.285, Si2p = 0.817) using the following formula according to Scofield libraries:[10]

$$PA_{corr} = \frac{PA_{exp}}{CS \cdot TXFN \cdot ECF}$$

where: PA_{corr} and PA_{exp} are the corrected and experimental peak areas, respectively, CS is the cross-section; TXFN is the transmission function (C1s = 16033, N1s = 16657, O1s = 17449, S2p = 15455, Cl2p = 15610, Si2p = 15149) and ECF is the energy compensation factor. In particular, TXFN is calculated from a polynomial fit to a plot of log[Peak area/PE · XSF] vs. log(KE/PE), where PE = pass energy; KE = kinetic energy and XSF is a relative sensitivity factor applied to normalize the two curves (mostly because of differences in photoelectron cross-section of different orbitals).

On the other hand, the ECF depends upon the library in use. In the case of the Scofield library the value corrects for the inelastic mean free path term and is equal to $KE^{0.6}$, where KE is the kinetic energy. Data were averaged over at least three analyzed points.

Preparation of the modified electrodes

Standard GC electrodes were mirror polished with alumina slurry. Residual alumina traces were removed by ultrasonication in a water bath. The preparation of the modified electrodes was already detailed.[4,5] However, the experimental conditions leading to optimal electrochemical performances, the same used to prepare the modified electrodes analyzed by XPS, are reported in Table 1[5] for facilitating the reading of the following paragraphs.

GC/ox electrodes were prepared under the same experimental conditions but in the absence of HQSA. Every experiment was performed by using a newly prepared electrode.

After the modification, both kinds of electrodes were slightly rinsed with water to remove unreacted species from the surface, and sealed under nitrogen atmosphere in test tubes to allow a safe transfer to the spectrometer. Immediately before the XPS analysis, they were cut to a maximum length of 0.8 cm to allow their positioning onto the sample rod and the insertion in the preparation chamber of spectrometer.

The HQSA powder was analyzed as received, by pressing it on a conductive adhesive copper tape.

Results and discussion

Voltammetric behavior

In Fig. 1 are reported the voltammograms relevant to the GC/HQSA and GC/ox electrodes in 0.04 M HCl solution.

The two patterns are characterized by noticeable differences. Broad peaks such as those present in the voltammetric profile relevant to GC/ox electrodes (dotted line in Fig. 1) were already

Table 1. Preparation of the HQSA-GCE and ox-GCE [5]

Parameter	HQSA-GCE	ox-GCE
HQSA concentration	10^{-3} M	0
Supporting electrolyte	0.04 M HCl	
Technique	cyclic voltammetry	
Cycles n°	10	
Scan rate	0.1 Vs^{-1}	
Negative potential limit	−1.5 V	
Positive potential limit	2.5 V	

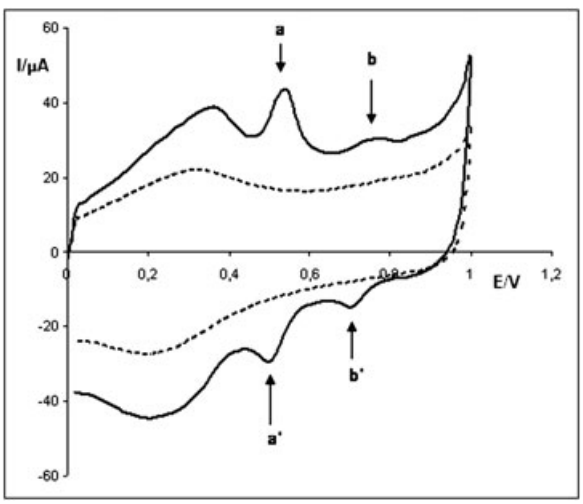

Figure 1. Comparison of typical cyclic voltammetric patterns relevant to GC/ox (dotted line) and GC/HQSA (solid line) electrodes, recorded in a 0.04 M HCl solution at 0.1 V/s.

reported in previous investigations relevant to electrochemically activated GC electrodes, and attributed to redox reactions of oxygen surface sites resulting from the applied electrochemical treatments.[6–9] The same broad peaks are still present, even if more intense, in the voltammogram recorded at GC/HQSA electrodes which, in addition, are characterized by two additional peak couples, a/a′ and, respectively, b/b′ attributed to HQSA redox intermediates.[4,5] It can be proved that the reaction pathway of HQSA at the GC/HQSA electrode is a surface confined redox process. In fact, a linear relationship was observed between the current relevant to the peak centered at about 0.74 V and the scan rate (test performed in the 0.01–0.2 Vs^{-1} range, $r^2 = 0.999$).[4,5]

Voltammetric profiles similar to the solid line in Fig. 1 (relevant to GC/HQSA electrodes) were recorded also at GC/ox electrodes dipped in a 10^{-3} M HQSA. However, in that case a linear relationship was observed between the current relevant to the HQSA peak centered at about 0.74 V and the square root of the scan rate (in the 0.01–0.1 Vs^{-1} range, $r^2 = 0.997$), thus indicating a diffusion-controlled process.[4,5] Then, it could be concluded that, under those experimental conditions, HQSA was not adsorbed onto the electrode surface but it remained in solution. In agreement with these evidences, transferring the same electrode in a HQSA-free supporting electrolyte solution caused the disappearance of the HQSA peaks system after only two scan cycles.[4,5]

As underlined above, all these results support the hypothesis that HQSA was adsorbed onto the electrode surface during the potential scan in HQSA-containing solutions but it could not be adsorbed by simply immersing a GC/ox electrode in HQSA-containing solutions after the electrochemical activation.[4,5]

X-ray photoelectron spectroscopy analysis

The survey scans relevant to GC/ox and GC/HQSA electrodes (prepared exactly in the same way as those used in electrochemical experiments) and an HQSA powder standard are reported in Fig. 2.

The scans relevant to GC/HQSA and GC/ox electrodes evidenced the presence of signals relevant to oxygen, carbon, nitrogen, silicon, and chlorine. The additional signal of sulfur was present only in the scan relevant to GC/HQSA electrode. The scan relevant to the HQSA powder evidenced the presence of signals relevant to oxygen, carbon, nitrogen, and sulfur.

Detailed scans of carbon, nitrogen, and sulfur are presented and discussed here. The O1s were not fitted because they are very unlikely differentiable in such complex specimens. The Si2p and Cl2p regions were not analyzed too, because the presence of silicon species on the electrode surface is likely ascribable to some unavoidable contamination during cutting the electrode tips and transfer to the spectrometer, while the presence of chlorine species is ascribable to the chloride containing supporting electrolyte used in electrochemical experiments.

Figure 3 shows an example of fit of the C1s region of GC/ox electrodes. The C1s spectrum may be split into five peak

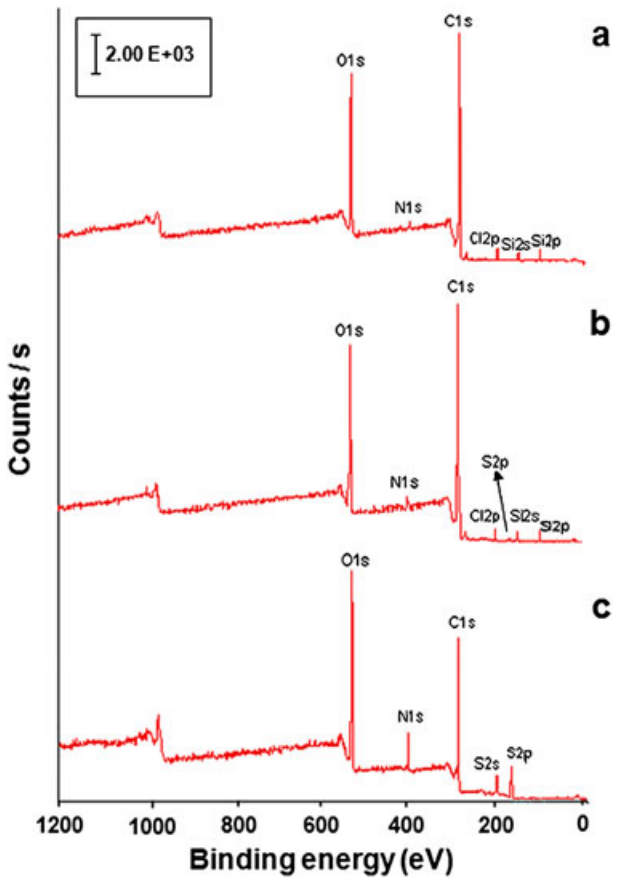

Figure 2. Survey scans relevant to (a) GC/ox electrodes, (b) GC/HQSA electrodes, and (c) HQSA powder.

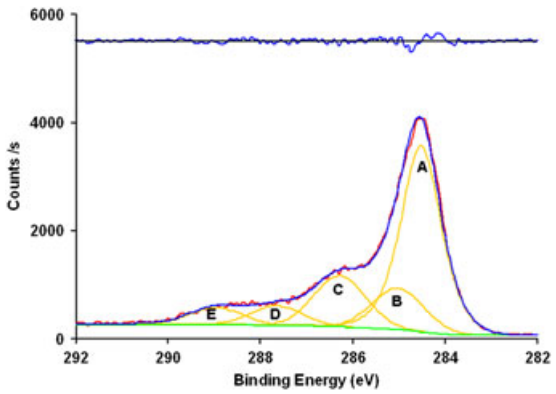

Figure 3. Example of fit of the C1s region of GC/ox electrodes. Peak attributions and binding energies are reported in the text.

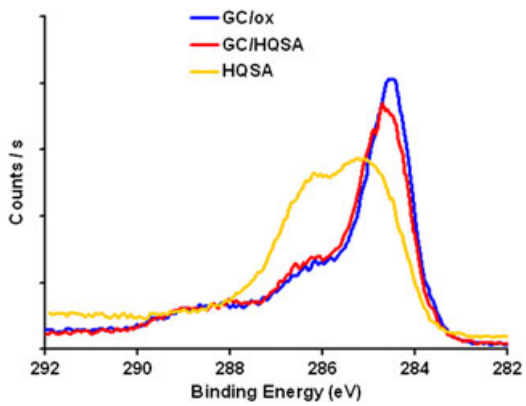

Figure 4. Comparison of the C1s regions of GC/ox and GC/HQSA electrodes and of HQSA powder.

components associated with the following species: peak A at 284.5 eV (C, graphite), peak B at 285.0 eV (CH_x), peak C at 286.3 eV (C–O), peak D at 287.7 eV (C = O) and peak E at 289.0 eV (COOH). The peak attributed to aliphatic carbon expresses also the contamination of the electrode surface as a result of adsorbed hydrocarbon monolayers.

The C1s regions of HQSA powder is reported in Fig. 4, where it can be compared with the same regions of the two investigated electrodes, GC/ox and GC/HQSA. It can be observed that the spectra relevant to the two electrodes show only slight differences because of the low amount of HQSA on the surface of the GC/HQSA system. This is in agreement with the electrochemical results suggesting that HQSA deposition could be uneven on the electrode surface, with more or less large void areas.[5]

Figures 5 and 6 show the N1s and S2p fits relevant to the three investigated samples. Figures 5(c) and 6(b) show the N1s and S2p fits relevant to the HQSA standard powder. The experimental BEs of the various peaks contributions (corrected for surface charging) are reported in Table 2. The relevant experimental atomic percents (at%) and atomic ratios are reported in Table 3. In this last table, theoretical ratios expected in the case of the HQSA powder are reported in parentheses beside experimental ones. The C/N atomic ratio, 10.6, is quite similar to the theoretical one (C/N = 9, as resulting from the chemical formula, $C_9H_7NO_4S$). The slight increase of the experimental value could well be due to some contamination of the powder surface as a result of adsorbed hydrocarbon monolayers in the analysis chamber of the spectrometer.

The experimental S/N and O/S ratios, respectively about 1.2 and 3.5, are slightly different from the theoretical ones, respectively 1.0 and 4.0. The results could be perhaps explained in terms of a somewhat moderate degradation of the powder under X-ray irradiation.

Assigning the BEs is quite uncertain. Most of the available $S2p_{3/2}$[11–17] and N1s[17–21] BEs reported in the literature are

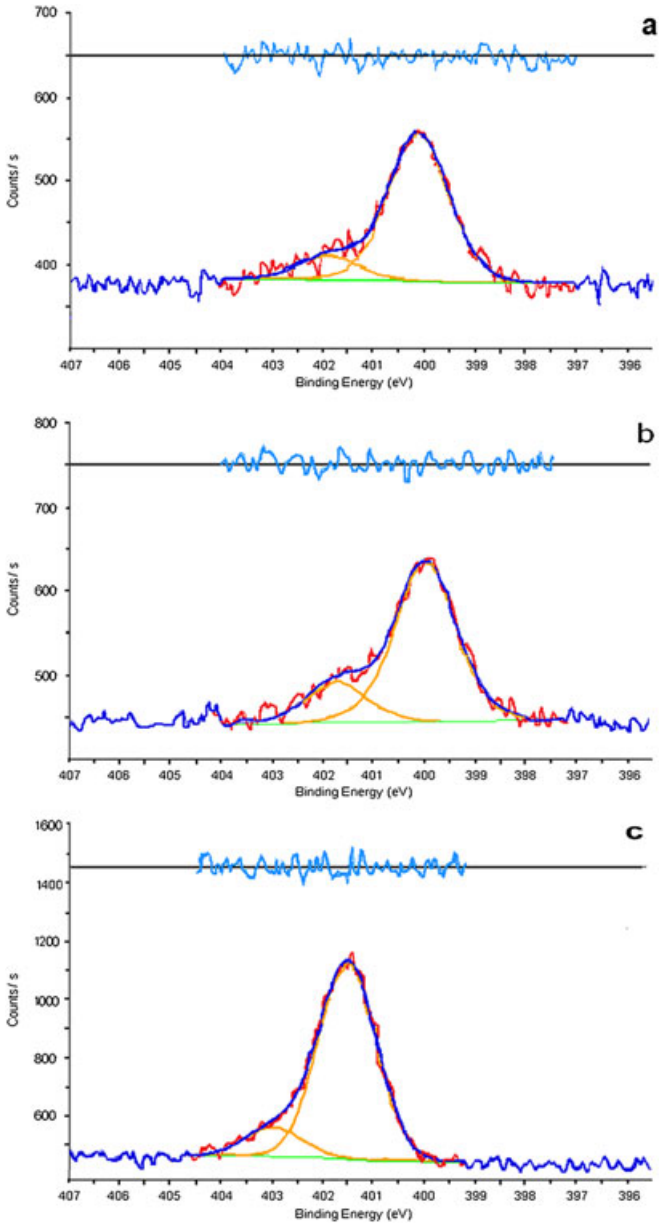

Figure 5. Comparison of fits of the N1s regions: (a) GC/ox electrodes, (b) GC/HQSA electrodes, and (c) HQSA powder.

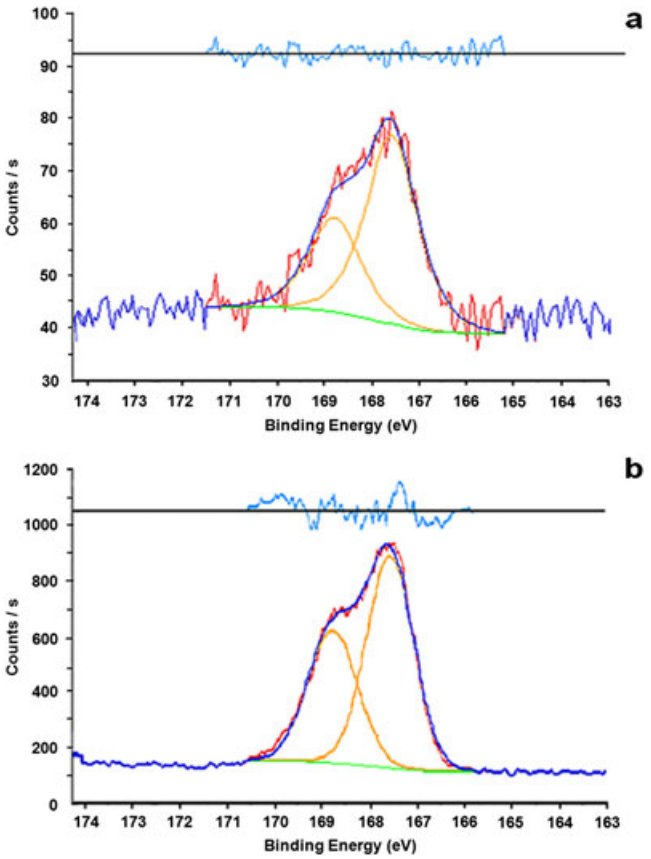

Figure 6. Comparison of fit of the S2p regions: (a) GC/HQSA electrodes and (b) HQSA powder.

Table 2. Comparison of BE values (eV) relevant to N1s and S2p regions of GC/ox and GC/HQSA electrodes and of HQSA powder

	Region	BE_1	BE_2
GC/ox	N1s	400.1	401.9
GC/HQSA	N1s	400.0	401.8
	$S2p_{3/2}$	167.6	
HQSA powder	N1s	401.6	403.0
	$S2p_{3/2}$	167.6	

Table 3. XPS results relevant to GC/ox and GC/HQSA electrodes and to HQSA powder

		Atomic percent	Experimental (theoretical) atomic ratios						
			C/N	S/N	O/S	O/C	S/C	Si/C	Cl/C
GC/ox	C	75.1 ± 0.3	37.6	—	—	0.24	—	0.04	0.03
	O	17.7 ± 0.9							
	N	2.0 ± 0.1							
	Si	3.2 ± 0.7							
	Cl	2.0 ± 0.5							
GC/HQSA	C	73.9 ± 0.6	33.6	0.18	44.8	0.24	0.005	0.04	0.03
	O	17.9 ± 0.4							
	N	2.2 ± 0.4							
	S	0.4 ± 0.1							
	Si	3.30 ± 0.01							
	Cl	2.3 ± 0.5							
HQSA	C	62.3 ± 0.5	10.6 (9.0)	1.2 (1.0)	3.5 (4.0)	0.4 (0.4)	0.11 (0.11)	—	—
	O	24.8 ± 0.5							
	N	5.9 ± 0.1							
	S	7.00 ± 0.04							

referenced to the C1s binding energy of surface hydrocarbon contamination taken equal to 284.5 eV,[11] 284.6 eV,[17] 285.0 eV (as made in the present work)[14,16,21] and 285.2 eV.[13] The $S2p_{3/2}$ BE at 167.6 eV of the unique 2p doublet assigned to sulfur, obtained by fitting the relevant detailed scan of the HQSA standard (see Fig. 6(b)) seems quite lower than that assigned to sulfonic groups present in the quite different matrices considered in the available references (from sulfonated styrene and styrene copolymers[13] to naphthol[1,8-*cd*]1,2-dithiole[14] to α-naphthalene sulfonate-doped polypyrrole[17] and to radiation grafted polytetrafluoroethylene-*g*-polystyrene sulfonic acid membranes[22]). Available data are 168.1 eV,[22] 168.3 eV,[13] 168.9 eV,[14,17] 170,0 eV.[22] Sulfates are reported around 168.3–169.5 eV.[11,16,23] These data suggest more or less important binding energy differences associated with the different molecular environments of sulfur atoms.

The N1s region of the analyzed HQSA powder, shown in Fig. 5(c), was resolved in two component peaks at 401.6 eV and 403.0 eV. Likely, it is possible assigning these contributions to polaron (a) and bipolaron (b) species:

the literature reports the relevant BEs at 401.0–401.1 eV (a) and, respectively, at 402.6–402.7 eV (b).[17,18] The BE of the N1s level in pyrrole, pyridine, pyrazine, and amino groups are definitively lower.[17–21]

Figures 5(a) and (b) show the high resolution XP spectra of the N1s region of the GC/ox and GC/HQSA electrodes, respectively. Table 2 allows comparing the BE values relevant to both kind of electrodes as obtained by fitting the relevant detailed scans. The N1s signal in Fig. 5(a), relevant to GC/ox electrodes, can be reasonably fit by two peaks at 400.1 eV and, respectively, at 401.9 eV. Also, the fit of the N1s region of GC/HQSA electrodes in Fig. 5(b) evidences the presence of two species. Their BEs are practically the same as those relevant to the N1s region of GC/ox electrodes, that is 400.0 and 401.8 eV, respectively. However, the ratios of the peak area at lower BEs to that at higher BEs decrease from 6.5 (GC/ox) to about 3.8 (GC/HQSA).

The increase of the peak at 401.8 eV in the GC/HQSA N1s region can be reasonably ascribed to the presence of HQSA. Indeed, in Fig.5(c), relevant to the HQSA powder, it can be observed that the main component of N1s signal of HQSA falls at 401.6 eV.

This hypothesis is also in agreement with the results of the analysis of the S2p region of GC/HQSA electrodes. See an example in Fig. 6(a). Its fit evidences the unresolved doublet because of the presence of the $S2p_{3/2}$ and $S2p_{1/2}$ components, characterized by a 2 : 1 peak area ratio and a 1.2 eV splitting. The relevant $S2p_{3/2}$ BE listed in Table 2, 167.6 eV, is perfectly equivalent to that relevant to the HQSA powder standard (see Table 2 and Fig. 6(b)) confirming that no/negligible modification in the HQSA properties occurred when this molecule was deposited onto the GC/HQSA electrode surface. Of course, as evidenced by survey scans, no signal ascribable to sulfur could be detected on the surface of GC/ox electrodes.

The atomic % (at%) and atomic ratios relevant to GC/ox and GC/HQSA electrodes are presented in Table 3. The at% of silicon and chlorine are only considered for allowing an estimation of the surface concentration of these contaminants.

The O/C ratio on both GC/ox and GC/HQSA electrodes is 0.24 (see Table 3). This value is somewhat larger than those usually assigned to untreated GC, e.g. 0.20–0.21 or lower,[24–26] but clearly lower than those reported for electrochemically oxidized GC electrodes, e.g. from about 0.27 up.[24,27] Of course, these differences can be at least in part explained by the different electrochemical treatments detailed in the cited papers.

The S/C ratio on the surface of GC/HQSA electrodes is quite low. Again, this seems in agreement with what was previously deduced by electrochemical experiments, that is by an uneven deposition of HQSA on the GC/HQSA electrode surface.[4,5]

Conclusions

The aim of this paper was to test the presence of sulfonic groups on the surface of the GC/HQSA electrodes. The obtained XPS results, even within the limits of conclusions drawn by analyses performed not *in situ*, confirmed that sulfur atoms, very likely pertaining to HQSA molecules, were present on the surface of GQ/HQSA electrodes. The $S2p_{3/2}$ BE relevant to these electrodes

(167.6 eV) is the same as that obtained for the HQSA powder standard. The observed differences between the BE value of the $S2p_{3/2}$ level of HQSA obtained in this work and those reported in the few available literature data can reasonably be ascribed to the very different chemical environments of the considered matrices.

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