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Please, find enclosed the manuscript “XPS characterization of glassy carbon electrodes chemically modified with 8-hydroxyquinoline-5-sulfonic acid” by B. Brunetti, E. De Giglio, D. Cafagna and myself. It is submitted for publication in Applied Surface Science.

Best regards
Elio Desimoni

This paper is aimed to elucidate the actual surface status of the presented modified electrode by using XPS, because this spectroscopic technique is the best suited for characterizing the first atomic/molecular surface layers onto electrode surface. The spectroscopic results, even if acquired *ex situ*, allowed confirming the presence of the hypothesized functional groups onto the surface of the proposed chemically modified electrode.

**XPS CHARACTERIZATION OF GLASSY CARBON ELECTRODES
CHEMICALLY MODIFIED WITH 8-HYDROXYQUINOLINE-5-SULFONIC ACID**

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ABSTRACT

A chemically modified glassy carbon (GC) electrode was prepared by cycling the potential in a wide range, in the presence of 8-hydroxyquinoline-5-sulfonic acid (HQSA). The electrode was successfully tested as a sensor of some species of alimentary and pharmaceutical interest. The performances of the modified electrode were improved 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. However, in the explored potential range, complex redox processes leading to the production of surface functional groups take place even at GC electrodes cycled in the absence of HQSA. In this respect, an XPS investigation was performed in order of better understanding the effective nature of active species present on the surface of HQSA modified electrodes. The experiments involved acquiring survey scans as well as detailed spectra of glassy carbon electrodes cycled both in the presence and in the absence of HQSA, as well as of an HQSA standard. The results of the qualitative and quantitative analysis of the spectra are discussed in the light of previous literature information.

Keywords:

Glassy carbon electrodes, 8-hydroxyquinoline-5-sulfonic acid, cyclic voltammetry, XPS, surface functionalities.

1. 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 [1-3]. Recently, a modified GC electrode was prepared by cycling the potential in an 8-hydroxyquinoline-5-sulfonic acid (HQSA) solution [4, 5]. The electrochemical characterization concerned with the optimisation of the deposition parameters of the surface modifier (HQSA concentration, negative and positive potential limits, number of cycles, nature and pH of the supporting electrolyte) by cyclic voltammetry experiments in dopamine test solutions [4, 5]. The HQSA modified electrode was applied as a sensor of some species of alimentary and pharmaceutical interest (dopamine, methylxanthines, food colorants, ascorbic acid). It could be shown that the above mentioned modification leads to significantly 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].

However, it is also known that cycling GC electrodes in such a wide potential range, but in the absence of HQSA, can also induce complex redox reactions on the electrode surface leading to electrochemically active surface functional groups, such as quinones, quinone-like, phenolic or alcoholic groups (see for example references 6-9). Moreover, HQSA could play the role of a catalyzer of functionalization reactions at the GC surface as well, without entering the actual surface chemistry of the electrode. Thus, an X-ray Photoelectron Spectroscopy (XPS) study was performed in order of elucidating the actual surface chemistry of the HQSA modified glassy carbon electrodes. The experiments involved the acquisition of wide and detailed scans relevant to GC electrodes cycled in the presence or in the absence of HQSA (GC/HQSA and GC/ox, respectively) and to a HQSA powder standard.

The results are presented and discussed in the light of previous literature information.

2. Materials and methods

2.1 Chemicals

Ultrapure water was obtained by passing house-distilled water through a Simplicity 185 (Millipore S.A., France) water purification system. 8-hydroxyquinoline-5-sulfonic acid (Sigma) and the other reagents were of analytical grade and used as received.

2.2 Instrumentation

Electrochemical experiments were performed by a model 1030 multipotentiostat (CH Instruments, Austin, TX, USA) connected to a PC. The three electrodes cell consisted of modified or bare glassy carbon 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 ($22 \pm 2^\circ\text{C}$).

The pH of the solutions was measured by a Thermo Orion, Model 420 pH meter.

XPS spectra were obtained with a ThermoVG Thetaprobe spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA, USA) equipped with a microspot monochromatised AlK α source. The AlK α line (1486.6 eV) was used throughout; the base pressure during acquisition of spectra was $2\text{-}3\cdot 10^{-9}$ mbar. The X-ray beam spot was 400 μm . The analysis was performed by acquiring survey scans (binding energy 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 Advantage software package, consisting of a non-linear least-squares fitting program. The experimental points of detailed spectra were fitted using Gaussian-Lorentzian peaks (85:15 ratio) having the same full width at half maximum. The maximum error on peak positions was + 0.2 eV. Charge referencing was done by setting the lower binding energy (BE) of C1s hydrocarbon photopeak at 285.0 eV. Quantification was done by peak area. The comparison of data from different elements was enabled by correction with empirically derived atomic sensitivity factors. Data were averaged over at least three points analyzed.

2.3 Preparation of the modified electrodes

The preparation of the modified electrodes was already detailed [4, 5]. However, the experimental conditions leading to optimal electrochemical performances are briefly reported here below for facilitating the reading of the following paragraphs.

Standard glassy carbon electrodes (disk diameter 2 mm, Metrohm, Herisau, CH) were mirror polished with alumina slurry. Residual alumina traces were removed by ultrasonication. According to the results of preliminary experiments, performed by cycling GC electrodes in different supporting electrolyte solutions containing concentrations of HQSA ranging from $1.0\cdot 10^{-3}$ M to $5.0\cdot 10^{-3}$ M [5], the best analytical results could be obtained in 0.04 M HCl containing $1.0\cdot 10^{-3}$ M HQSA. Thus, the GC/HQSA electrodes examined in the present work were prepared by applying 10 cycles between -1.5V and 2.5 V, at 0.1 Vs^{-1} , to a GC electrode dipped in 0.04 M HCl containing $1.0\cdot 10^{-3}$ M HQSA [4, 5].

GC/ox electrodes were prepared under the same experimental conditions but in the absence of HQSA. After the modification, the electrodes were rinsed with ethanol and water to remove unreacted species from their surface.

GC/HQSA and GC/ox electrodes were stored under nitrogen atmosphere and, after cutting them to a maximum length of 0.8 cm (for allowing the insertion in the spectrometer) transferred to the preparation chamber of the XPS instrument.

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

3. Results and discussion

3.1 Voltammetric behaviour

Representative cyclic voltammetric patterns relevant to GC/ox and GC/HQSA electrodes, as those prepared for XPS investigations, are presented in Figure 1. The displayed voltammograms, recorded in a 0.04 M HCl support electrolyte, are those obtained after ten cycles at 0.1 V s^{-1} . The two patterns are characterized by noticeable differences. Broad peaks such those present in the voltammetric profile relevant to GC/ox electrodes (dotted line in Figure 1) were already reported in previous investigations relevant to electrochemically activated GC electrodes, and attributed to redox reactions of oxygen surface sites resulting from the applied electrochemical treatment [6-9].

The same broad peaks are still present, even if more intense, in the voltammogram recorded at GC/HQSA electrodes which, in addition, is characterized by two additional anodic peaks around 0.54 V and 0.76 V [4, 5].

Please insert here Figure 1

3.2.1 XPS analysis of HQSA powder

The experimental binding energies (corrected for surface charging) and the experimental atomic percents (At%) and ratios recorded on HQSA standard powder are presented in Table 1. The C/N atomic ratio, 9.9 ± 0.6 , is quite similar to the theoretical one (C/N = 9) as resulting from the chemical formula, $\text{C}_9\text{H}_7\text{NO}_4\text{S}$. The slight increase of the experimental value could well be due to contamination of powder surface as a result of adsorbed hydrocarbons monolayers. But the experimental S/N and O/S ratios, respectively about 1.5 and 2.7, are quite different from the theoretical ones, respectively 1.0 and 4.0.

Assigning the binding energies is quite uncertain. Most of the available S2p_{3/2} [10-16] and N1s and [16-20] BEs reported in the literature are referenced to the C1s binding energy of surface hydrocarbon contamination taken equal to 284.5 [10], 284.6 eV [16], 285.0 eV (as made in the present work) [13, 15, 20] and 285.2 eV [12]. In the present work, the S2p_{3/2} BE observed at 167.6 eV for the HQSA standard seems quite lower than that usually assigned to sulfonic groups, that is 168.1 eV [21], 168.3 eV [12], 168.9 eV [13, 16] and to sulfates, which is reported around 168.3-169.5 eV [10, 15, 21].

The N1s region of the analyzed HQSA was resolved in two component peaks at 401.6 eV and 403.0 eV. See Figure 2. Likely it is possible assigning these contributions to polaron (-NH^{•+}) and bipolaron (=NH^{•+}) species: the literature reports the relevant BEs at 401.0-401.1 eV and, respectively, at 402.6-402.7 eV [16, 17]. The BE of the N1s level in pyrrole, pyridine, pyrazine and amino groups are definitively lower [16-20].

These finding seems suggesting some degradation of the compound under vacuum/irradiation conditions. A reasonable hypothesis is, at least, a partial loss of some NO_x species.

Please insert here Figure 2

3.2.2 XPS analysis of GC/HQSA and GC/ox electrodes

Survey scans relevant to GC/HQSA electrodes evidenced the presence of signals relevant to oxygen, carbon, nitrogen, sulfur, silicon and chlorine. The same but S2p were also evidenced in survey scans relevant to GC/ox electrode.

The Si2p and Cl2p signals were not fitted in the following discussion. This because the first is likely ascribable to some unavoidable contamination during cutting the electrode tips and transfers to the spectrometer, while the second is clearly ascribable to the chloride containing supporting electrolyte used in electrochemical experiments. Their atomic percent are only considered in Table 2 for allowing an estimation of their surface concentration.

The atomic percent, At%, and atomic ratios relevant to GC/HQSA and GC/ox electrode are presented in Table 2 and Table 3, respectively. The O/C ratio on both GC/ox and GC/HQSA electrodes is 0.24. This value is somewhat larger than those usually assigned to untreated GC, e.g. 0.20-0.21 or lower [23-25], but clearly lower than those reported for electrochemically oxidized GC electrodes, e.g. from about 0.27 up [23, 26]. Of course, these comparisons should also take into account the different electrode treatments detailed in the cited papers.

The S/C ratio on the surface of GC/HQSA electrodes is quite low. It is possible that this could be due to some losses under UHV conditions.

Figure 3 allows comparing the C1s regions of GC/ox and GC/HQSA electrodes. These regions were not fitted since, at least from the point of view of surface chemistry, the slight difference between the spectra relevant to the two electrodes, as evidenced by the figures, is hardly significant.

Please insert here Figure 3

The wide scans relevant to the two electrodes displayed the signals of carbon, oxygen and nitrogen. Sulphur was only present in the wide scan of GC/HQSA. Table 4 shows the BEs obtained by fitting the relevant detail scans. Also the O1s detail scans and O/C ratios of the two electrodes did not show appreciable differences. Since also fitting the O1s regions could not add any useful information, the relevant data were omitted in this paper. Table 4 shows the BEs estimated for the two kinds of electrodes.

Figures 4A and 4B show the high resolution XP spectra of the N1s region of the GC/ox and GC/HQSA electrodes, respectively. Figure 4A, relevant to GC/ox electrodes, can be reasonably fit by a single peak at 400.7 eV (see Table 4). On the contrary, the fit of the N1s region of GC/HQSA electrodes in Figure 4B evidences the presence of two species. The first is characterised by a BE of 400.6 eV while the second one has a BE of 402.4 eV. The first one is likely coincident with that appearing at the same binding energy in the correspondent region of the GC/ox electrode. The second one, at higher binding energies (402.4 eV) can be attributed to positively charged nitrogen atoms of HQSA.

Please insert here Figures 4 and 5

Of course, no signal ascribable to sulphur could be detected on the surface of GC/ox electrodes. Figure 5 shows an example of the high resolution XP spectra of the S2p region of GC/HQSA electrodes. Its fit evidences the unresolved doublet due to 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 4, 168.2 eV, is clearly higher than that relevant to the HQSA standard (167.6 eV, see Table 1) and seem more consistent with the presence onto the GC/HQSA surface of sulphur atoms involved in sulfonic acid groups.

4. Conclusions

The aim of this paper was testing the presence of sulfonic groups onto the surface of the GC/HQSA electrodes.

The obtained XPS results, even within the limits of conclusion drawn by analyses performed not *in situ*, confirmed that sulphur atoms were present on the surface of GQ/HQSA electrodes.

The comparison with the results of the analysis of the HQSA powder standard indicated that sulphur atoms, on the electrode surface, are present in a more oxidized status than those present on the surface of the X-ray irradiated HQSA standard.

For what concerns the analysis of the powder, the observed S2p_{3/2} BE (167,6 eV) definitely lower than the theoretical value assignable to sulfonic groups (168.1-168.9 eV) and the S/N and O/S atomic ratios significantly different from theoretical, can probably be explained by some degradation under UHV irradiation. On the contrary, the S2p_{3/2} BE relevant to the GC/HQSA electrode (168.2 eV) is reasonably close to that reported for sulfonic groups, and could be explained in terms of some stabilization of these functionalities during the potential cycling procedure.

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Caption to figures

Fig. 1. Comparison of typical cyclic voltammetric patterns relevant to GC/ox (dotted line) and GC/HQSA (solid line) electrodes. The voltammograms, recorded in a 0.04 M HCl support electrolyte, are those obtained after ten cycles at 0.1 V s^{-1} .

Fig. 2. High resolution XP spectrum of N1s region of the HQSA standard

Fig. 3. Comparison of the C1s regions of GC/ox and GC/HQSA electrodes.

Fig. 4. Comparison of fits of the N1s regions of GC/ox (a) and GC/HQSA (b) electrodes.

Fig. 5. Example of fit of the S2p regions of GC/HQSA electrodes.

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Figure 1
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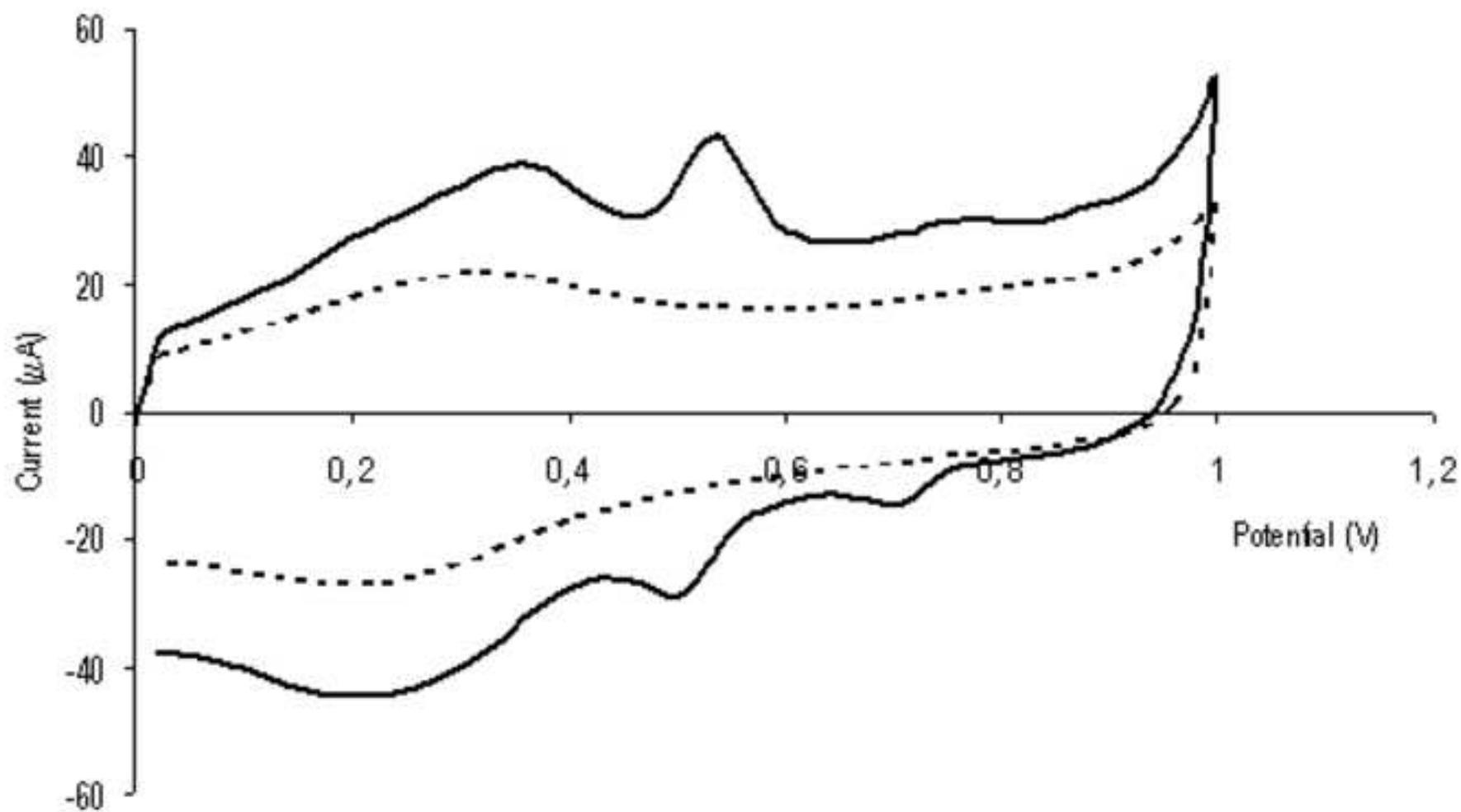


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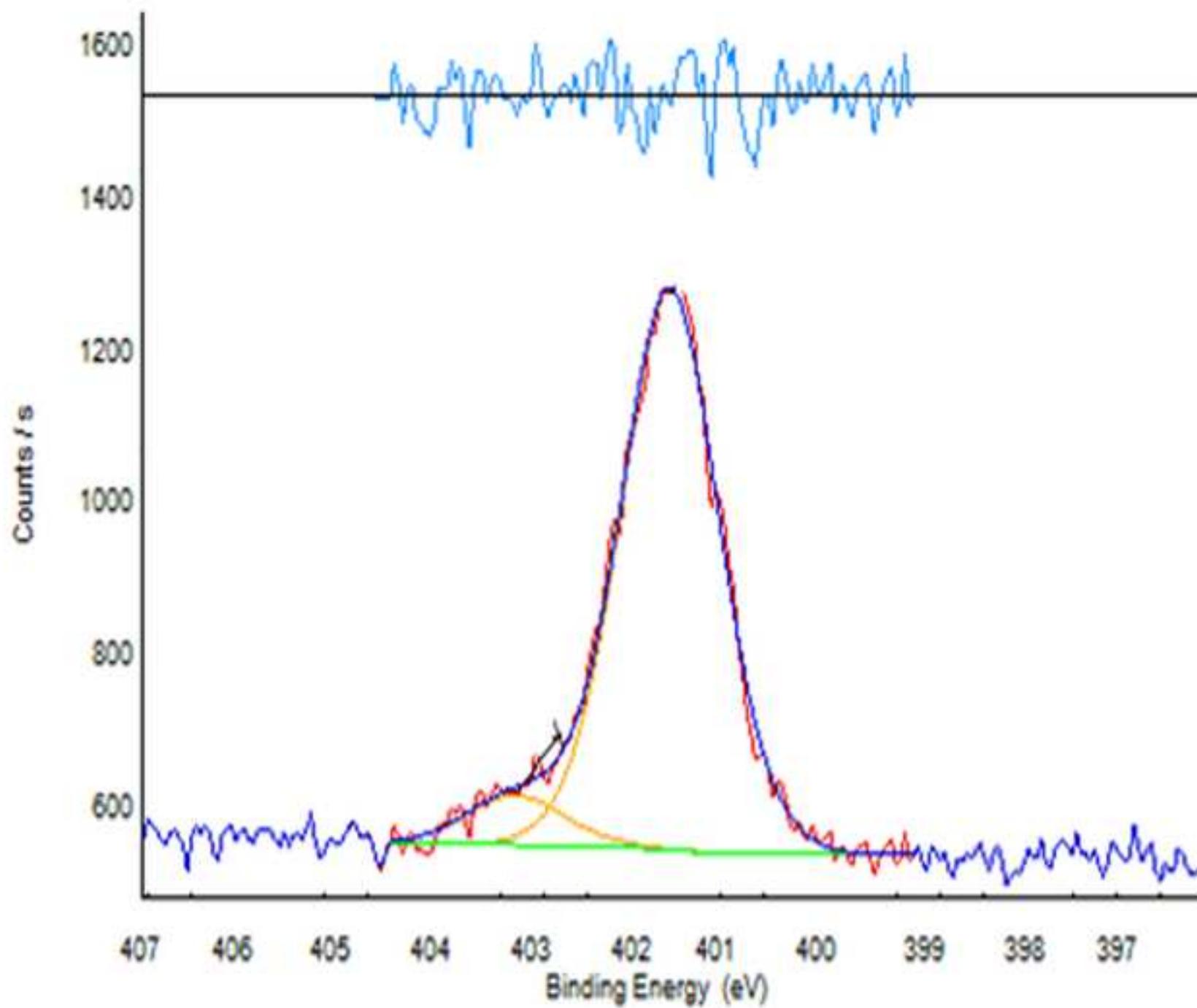


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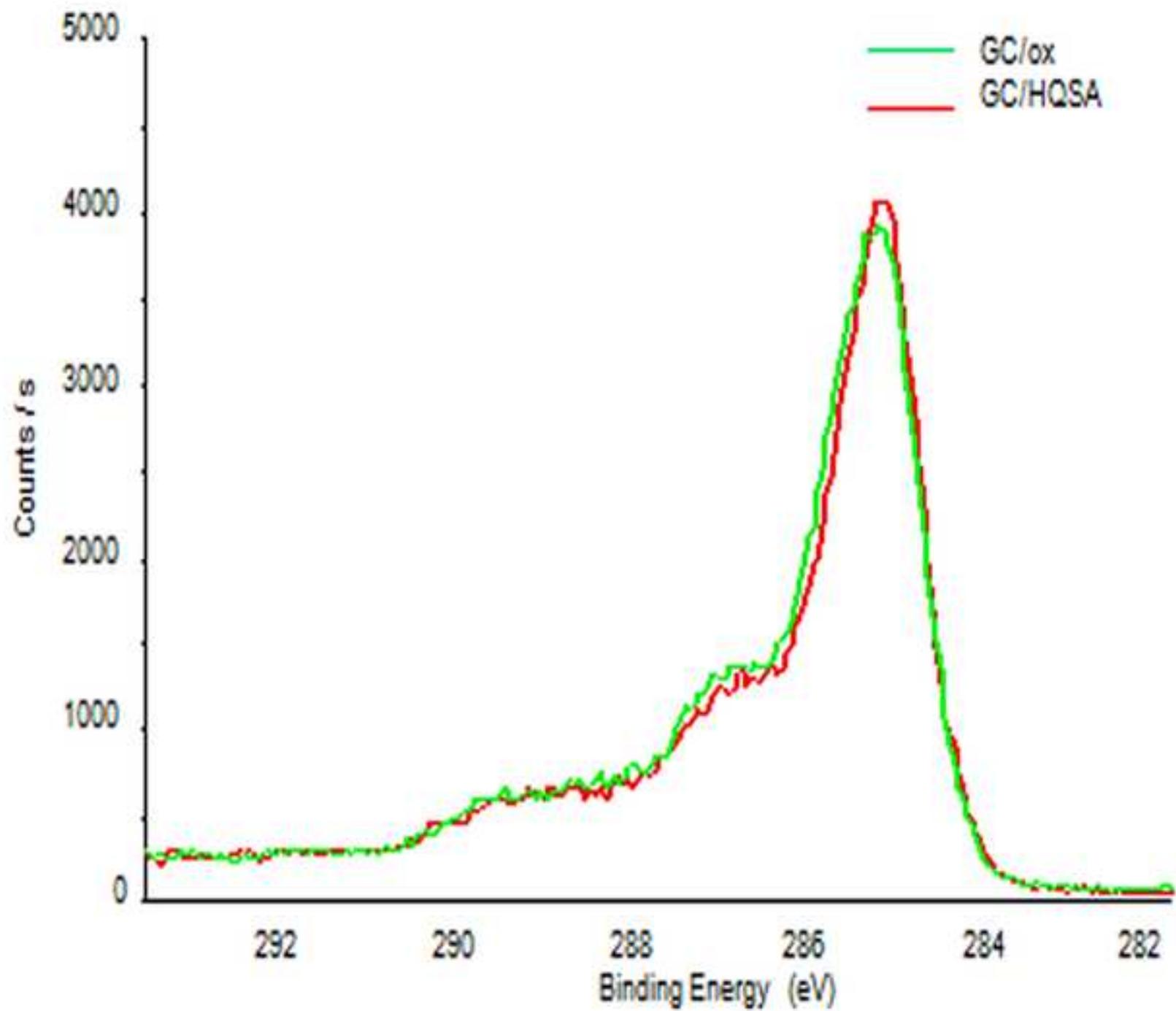


Figure 4

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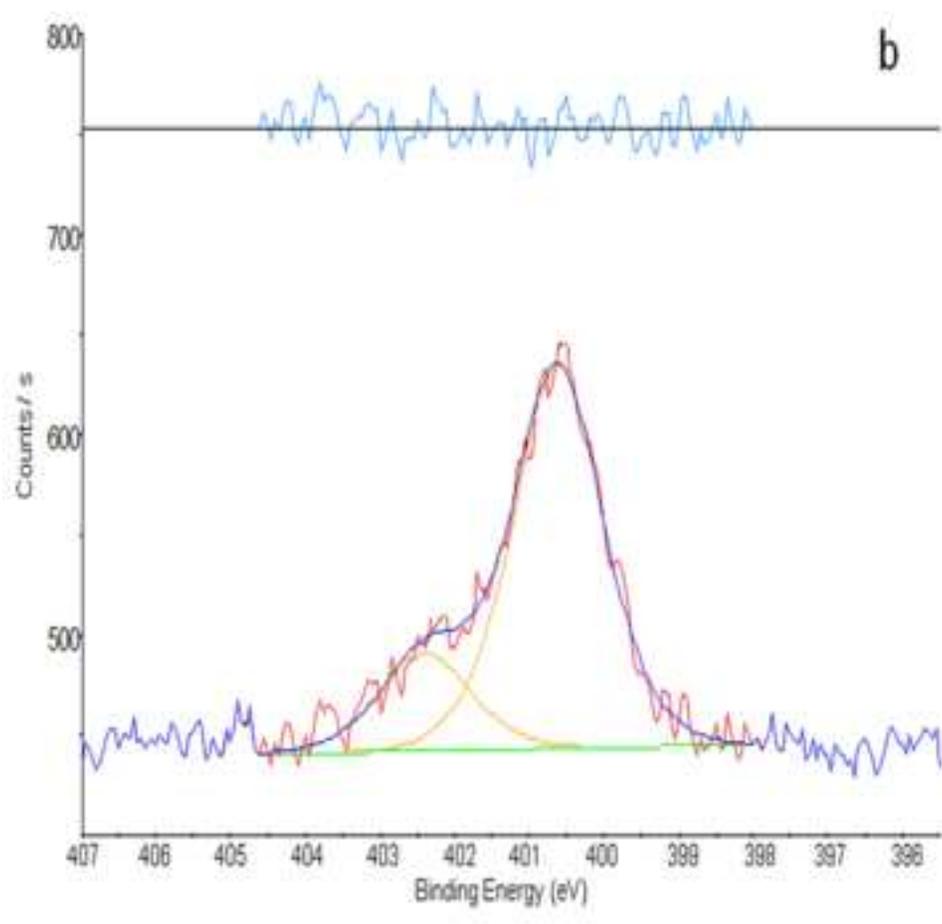
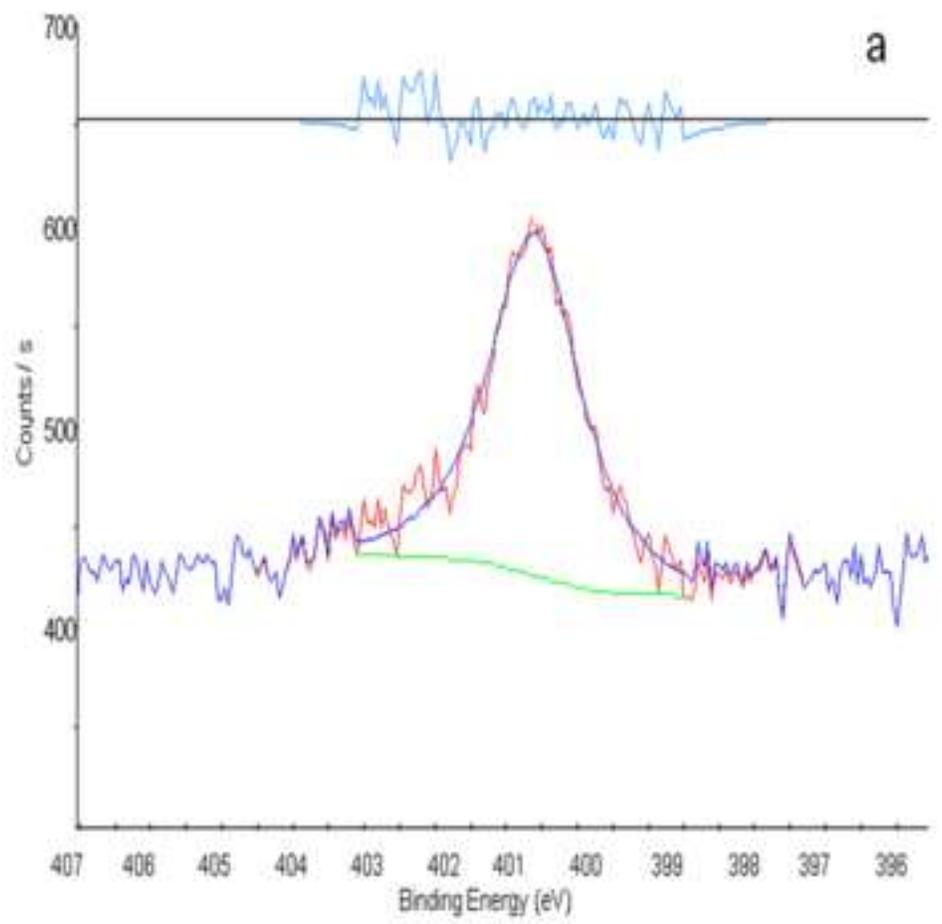


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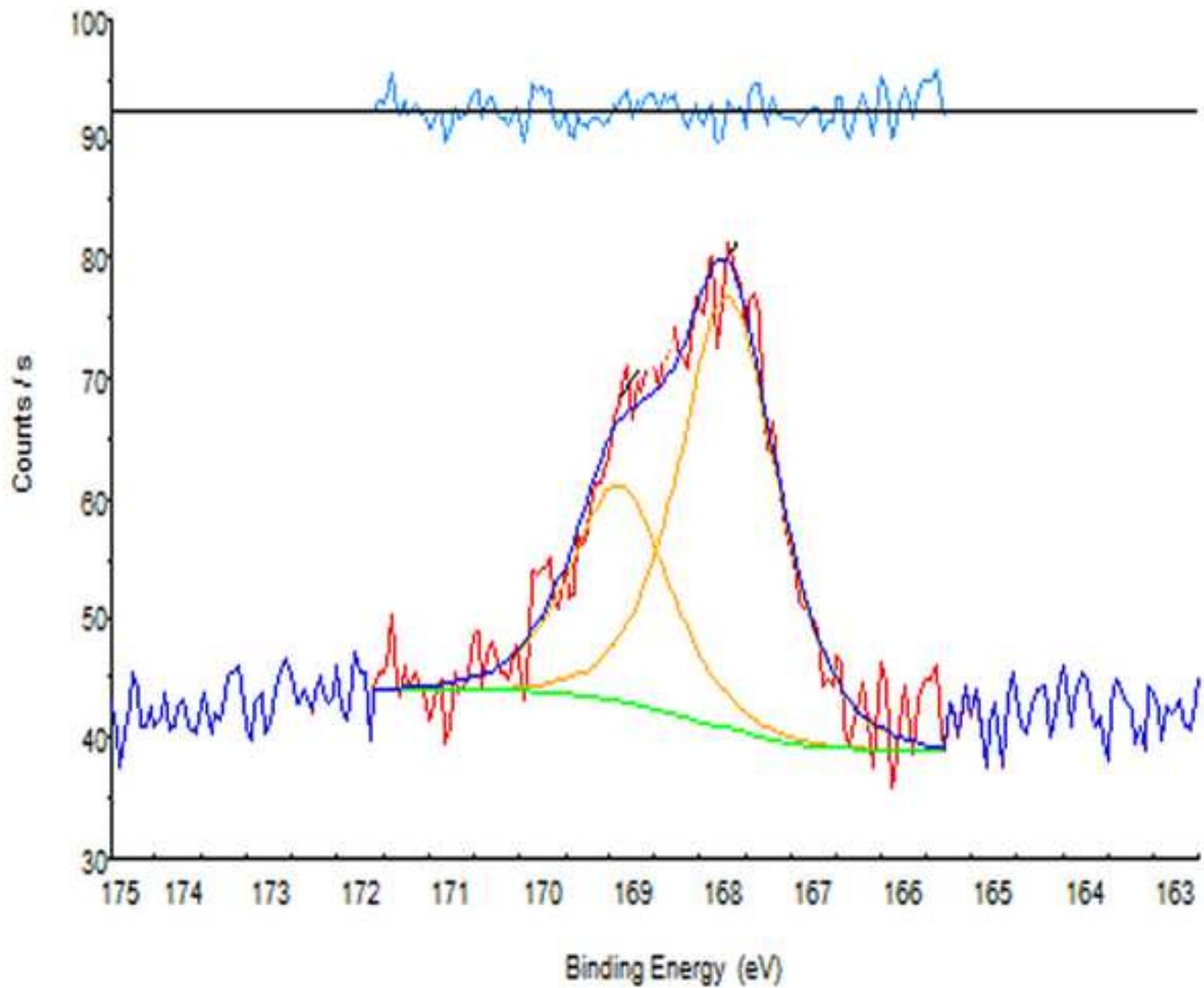


Table 1

XPS results relevant to the HQSA powder

Binding energies			Atomic percent				Atomic ratios			
C1s	N1s	S2p _{3/2}	C	O	N	S	C/N	S/N	O/S	O/C
285.0	401.6 403.0	167.6	60.5	24.3	6.1	9.1	9.9	1.5	2.7	0.4

Table 2
XPS results relevant to GC/HQSA electrodes

	Atomic percent	Atomic ratios						
		C/N	S/N	O/S	O/C	S/C	Si/C	Cl/C
C	74.0							
O	17.6							
N	2.4	31	0.21	35	0.24	0.007	0.04	0.03
S	0.5							
Si	3.2							
Cl	2.3							

Table 3
XPS results relevant to GC/ox electrodes

	Atomic percent	Atomic ratios	
		C/N	O/C
C	75.1		
O	17.7	38.5	0.24
N	2.0		

Table 4
Comparison of BE values relevant to GC/ox and
GC/HQSA electrodes

	Region	BE ₁	BE ₂
GC/ox	C1s	285.0	
	N1s	400.7	
GC/HQSA	C1s	285.0	
	N1s	400.6	402.4
	S2p _{3/2}	168.2	
