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Differential pulse voltammetric determination of the carcinogenic diamine 4,4'-oxydianiline by electrochemical preconcentration on a MoS₂ based sensor

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Abstract

We present an electrochemical sensor towards 4,4'-oxydianiline (Oxy) determination based on the ability of MoS₂ for diamine adsorption and preconcentration. It consists of a glassy carbon electrode covered by drop-casting with MoS₂ nanosheets obtained by exfoliation in 45% EtOH/H₂O mixture. X-Ray Photoemission Spectroscopy indicates that Oxy accumulates on the MoS₂ surface through an electropolymerization process similar to that reported for aniline. We use both, electrochemical impedance spectroscopy and atomic force microscopy for the characterization of the electrode surfaces at the different stages of the device fabrication. The electrochemical sensor allows the detection of Oxy at 8×10^{-8} M level with Er (%) and RSD (%) values lower than 8.3 and 5.6, respectively, in all the concentration range assayed. The methodology proposed was applied to the selective Oxy determination in real river water samples, showing very good selectivity and recoveries of around 95% in average.

Keynotes

Transition metal dichalcogenides; electrochemical detection; 4-4'Oxydianiline preconcentration; X-ray photoemission spectroscopy; atomic force microscopy

1 Introduction

Two-dimensional (2D) materials, mainly graphene, have proved to be a great choice for the development of new electrochemical sensors in order to respond to the social demands for more powerful analytical tools. [1] In this sense, literature reports their use as modifier of electrode surfaces, either alone or in combination with different materials as nanoparticles or enzymes. [2–4] More recently, transition metal dichalcogenides (TMDs) have emerged as

new materials beyond graphene with interesting and promising applications. [5, 6] Among TMDs, the most studied and employed is molybdenum disulphide (MoS_2), which presents a laminar structure composed of Van der Waals-stabilized layers of Mo atoms covalently bound to six S atoms. [7] In order to obtain nanosheets of MoS_2 , different synthesis procedures can be followed. [8, 9] MoS_2 can be obtained following bottom-up protocols from molybdenum metal salts and organic compounds with sulphur groups [10] or top-down approaches which are usually based on breaking the Van der Waals interaction between the MoS_2 layers. To this end, liquid exfoliation with adequate solvents [9, 11] or the intercalation of ions as lithium [12] between the layers are the procedures usually selected.

Although MoS_2 has been mainly employed for optoelectronics, generation and storage of energy [13, 14] and battery applications, [15, 16] the benefits of using this low dimensional nanomaterial in the development of analytical sensors are still scarcely explored. In a review, Sinha and co-workers summarize different strategies based on the utilization of MoS_2 for the detection of multidisciplinary targets as biomolecules, food ingredients, pharmaceutical, environmental contaminants and explosives [7]. Most of the works related to the development of electrochemical sensors are based on the modification of a conventional electrode surface with hybrid structures of MoS_2 and other nanomaterial as metal nanoparticles [17–20], graphene [21–23], conductive polymers [24], or carbon nanotubes. [25, 26] Our group has recently demonstrated the synergistic effect between MoS_2 nanosheets and diamond nanoparticles in the design of an electrochemical sensor for the determination of the anticonvulsant valproic acid [27]. Moreover, we have also obtained excellent results in the development of MoS_2 biosensors for lactate determination. [28] However, just a few examples of electrochemical sensors exclusively based on the use of MoS_2 layers can be found in literature. [10, 29, 30]

One of the most important uses of aromatic diamines is the manufacturing of polymers and membranes. However, these compounds are reasonably anticipated to be human carcinogen [31]. In particular, 4,4'-Oxydianiline (Oxy), with demonstrated high toxicity, is one of these aromatic diamines widely used also in dyeing processes of leather manufacturing. [32–34]. Due to the high possibility of Oxy to be released to wastewaters, its monitoring is a relevant issue to attend. Most of the analytical methods developed for Oxy determination are based on chromatographic techniques with UV or MS detection. [35–38] However, despite of its simplicity and high sensitivity, electrochemical techniques are scarcely employed for Oxy determination [39, 40].

In this work, we show that MoS_2 nanosheets, obtained by liquid exfoliation and directly deposited on a glassy carbon electrode (GCE) surface, allow for the development of a TMD-based electrochemical sensor able to accumulate the diamine onto the electrode surface in an extraction-like step from the sample, for the subsequent Oxy determination in a selective and sensitive process.

2 Experimental

2.1 Reagents

Molybdenum disulphide (MoS_2) (99%, 90 nm powder), ethanol absolute (EtOH) (99%), methanol, potassium ferrocyanide and potassium ferricyanide were obtained from Sigma Aldrich (www.sigmaaldrich.com). 4,4'-Oxydianiline (Oxy), 4,4'-Thiodianiline (Thio) and 4,4'-Diaminodiphenyl amine (Ddp) were purchased from Fluka (www.lab-honeywell.com). Sodium phosphate, sodium acetate and sodium borate (Sigma Aldrich, www.sigmaaldrich.com) were used for preparing buffer solutions in the 2-12 pH range.

2.2 Instrumentation

Electrochemical measurements were carried out with a μ -Autolab Type III potentiostat employing GPES software (both from Metrohm Autolab, Utrecht, Netherlands, www.ecochemie.nl). Electrochemical Impedance Spectroscopy (EIS) was performed with a Frequency Response Analyzer (FRAII) from Eco-Chemie coupled with the potentiostat.

The Atomic Force Microscopy measurements (AFM) were performed in air with an Agilent 5500 PicoPlus (Agilent) system. The images were taken in the dynamic mode using silicon cantilevers (Bruker, www.bruker.com) with a nominal force constant of 40 N/m and a nominal radius of 8 nm. Usually, large areas (around $64 \mu\text{m}^2$) were scanned in order to have a general view of the overall morphology. In some cases, higher resolution images were also obtained. In any case, the large images consisted of 2048×2048 pixels, which allow zooming smaller areas with enough resolution. It is worth noting that different cantilevers were employed in order to discard tip artefacts in the imaged structures. The phase contrast image was also recorded simultaneously to the topographical one, which proved to be useful to distinguish between the different components of the final sensor (see below).

X-ray photoemission spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of 1.0×10^{-10} mbar. The chamber is equipped with a PHOIBOS 100 - 1D delay line detector electron/ion analyser and a monochromatic Al K α anode (1486.6 eV). All spectra were measured with a pass energy of 15 eV and binding energies (BE) were calibrated to carbon C 1s core level peak at 285.0 eV. Voigt functions were used during the peak fitting after Shirley-type background subtraction. Lorentzian full-width half-maximum (FWHM-L) was kept constant for each element during the fitting (0.15 and 0.35 eV for N and O, respectively), while the Gaussian width (FWHM-G) was allowed to vary.

2.3 Procedures

MoS_2 nanosheets are prepared by top-down solvent exfoliation following a procedure previously described [27, 28]: 75 mg of MoS_2 are exfoliated in 10 mL EtOH/ H_2O (45%, v/v) by bath ultrasonication during 2 h. After 24 h at 4°C, the suspension is centrifuged at 1500 rpm for 45 minutes. Finally, the supernatant is separated and stored at 4°C. This suspension was further diluted (60% dilution in 45% EtOH/ H_2O) and employed to modify glassy carbon electrodes (for electrochemical measurements) or glassy carbon rod surfaces (for

AFM and XPS measurements). The modification consisted in placing 6 μL of the suspension on the surface and air-drying at room temperature.

The electrochemical measurements were performed using a three-electrodes cell including a Ag/AgCl/KCl (3M) reference electrode, a GCE-MoS₂ as working electrode and a platinum wire as the counter one. Differential pulse voltammetry (DPV) measurements were carried out from 0.0 to 0.5 V, in 0.1 M acetic acid buffer pH 5 as supporting electrolyte, after an accumulation step at 0.6 V during 360 s. The scan rate and the pulse amplitude employed were 10 mV/s and 60 mV, respectively. Electrochemical impedance spectroscopy measurements were carried out in 0.1 M phosphate buffer solution at pH 7 containing 10.0 mM K₃Fe(CN)₆/K₄Fe(CN)₆. A sinusoidal potential modulation of ± 10 mV amplitude over the open circuit potential (OCP) of the redox couple ($E_{\text{ocp}} = 0.22$ V) was applied in the 10^5 Hz – 10^{-2} Hz frequency range.

For AFM and XPS experiments, GCE/Oxy and GCE/MoS₂/Oxy samples were prepared by immersing a GCE or a GCE/MoS₂ rod in a 1×10^{-4} M Oxy solution (prepared in a 0.1 M AcH/Ac⁻, pH 5) and recording 15 cyclic voltammetry scans between 0.0 and 0.8 V at 0.1 mV/s.

The performance of the proposed method was evaluated by the Oxy determination in river water samples from Zánacara River (Camino Dique Mol, Villar de Cañas, Cuenca, Spain). Sample aliquots of 4.0 mL were spiked at different Oxy concentration levels in the $0.3 \cdot 10^{-6}$ M to $0.7 \cdot 10^{-6}$ M range, filtered through a 0.45 μm syringe filter and diluted to 20.0 mL in supporting electrolyte before analysis.

3 Results and discussion

3.1 Oxy electrochemical response. Cyclic voltammetry experiments

Cyclic voltammetry (CV) assays were performed in order to study the electrochemical response of the analyte with the modified electrode (GCE/MoS₂). Fig. 1A shows the successive cyclic voltammograms obtained with a GCE/MoS₂ electrode in a 0.1 mM Oxy solution (voltammograms b to f) in comparison with the signal corresponding to the supporting electrolyte (voltammogram a). As observed, an oxidation wave at 0.62 V appears in the first scan (voltammogram b). In the subsequent potential scans, a new redox pair with oxidation and reduction waves at lower potential values (0.27 V) are registered. These new signals only appear after applying a potential higher than 0.5 V, the latter increasing their intensity with successive cycles (voltammograms c to f). Moreover, we tested that after different consecutive potential scans in Oxy solution, the cyclic voltammogram obtained in a supporting electrolyte free of Oxy (Fig. 1B) just shows the oxidation and reduction waves corresponding to this new redox pair. Considering these results, this new electrochemical system can be attributed to a compound resulting from the Oxy oxidation that remains adsorbed onto the electrode surface. This point will be elucidated later from electrochemical and XPS experiments. Then, the analysis of the target can be carried out following the intensity at this new peak, which appears at lower and more selective potential.

As observed in the inset of Fig. 1B, where the oxidation current is plotted, the redox signal corresponding to the pair at 0.27 V increases with the number of cycles but only up to 15 scans. Although this behaviour is observed for both the modified and the bare electrode, it is important to note that a 40% higher oxidation intensity is recorded when MoS₂ is present. If the potential is cycled for more than 15 times, the charge transfer is impeded, and the signal begins to decrease because of the thickness of the film formed.

To support the hypothesis that the Oxy oxidation product is adsorbed on the MoS₂ surface, we studied the influence of the scan rate (v) in the peak current. To this end, once the potential is scanned between 0.0 and 0.8 V in a 0.1 mM Oxy solution for 14 cycles, the scan number 15 was recorded from 0.0 to 0.45 V at different v values in the same solution. The results (Fig. S1A) showed that the oxidation wave current at 0.27 V increases linearly with the scan rate according to $I_p \text{ (A)} = -9.76 \times 10^{-9} + 1.08 \times 10^{-8} v \text{ (mV s}^{-1}\text{)}$, $r = 0.994$. If the $\log I_p$ vs. $\log v$ plot is obtained from these data (Fig. S1B), a linear relationship with a slope close to 1 is obtained ($\log I_p = -7.93 + 0.97 \log v$, $r = 0.996$). These results confirm that MoS₂ is able to accumulate the Oxy oxidation product in an adsorption process. Because of that evidence, a relevant parameter to consider is the amount of MoS₂ incorporated on the electrode surface. Therefore, the exfoliated suspension (7.5 mg/mL) was diluted to 1.5, 3.0, 4.5 and 6.0 mg/mL and 6 μ L of these later suspensions were employed to modify the electrode surface. The results, depicted in Fig. S2, showed that the oxidation current increases with the MoS₂ amount up to 4.5 mg/mL. Moreover, amounts of MoS₂ on the electrode surface higher than 6.0 mg/mL seem to impede the electrochemical process, leading to lower intensity currents because of the thickness of the film. Therefore, further assays were carried out by drop-casting 6 μ L of 4.5 mg/mL MoS₂ on the electrode surface.

3.2 XPS characterization

In order to corroborate the presence of an Oxy derivative on the electrode surface and to elucidate the nature of such compound, responsible for the redox pair at +0.27 V, XPS measurements were performed. For this purpose, three different samples were studied, namely Oxy deposited on the GCE surface by drop-cast (Oxy, as reference), Oxy deposited on the GCE surface after 15 cyclic voltammetric scans and Oxy deposited after 15 cyclic voltammetric scans onto the MoS₂ modified electrode.

Fig. 2A shows the molecular structure of Oxy. Attending to this structure and according to available literature for electropolymerization of other related compounds such as aniline [41], the Oxy oxidation product obtained upon several electrochemical cycles is expected to be the result of intermolecular coupling of the cation radical monomers leading to hydrazobenzene. To confirm this hypothesis, the N 1s and the O 1s core level peaks have been characterized by XPS. Fig. 2B shows the corresponding N 1s core level peak for the three different samples, together with their deconvoluted species. Drop-casted Oxy/GCE can be considered as the reference spectrum for the molecule as a multilayer coverage is expected. In this case, the N 1s peak is composed by just a single component located at 400.1 eV, characteristic of NH₂ groups, [42, 43] thus indicating the integrity of the amino functional group upon deposition on the surface. In the same way, Fig. 2C shows the corresponding deconvoluted O 1s core level peaks. In this case, two components are

observed for the Oxy/GCE drop-cast sample. The more intense one appears at 532.4 eV, while the less intense one is located at 533.7 eV. The latter peak is characteristic of oxygen atoms attached to phenyl rings as one would expect for Oxy molecule,[44] while the former one is typically associated to oxygen in aliphatic compounds, probably associated to the solvent used. [45] Thus, summing up both spectra, it can be unambiguously stated that the Oxy molecules remain intact on the surface of GCE. The XPS spectra of the Oxy/GCE sample obtained after 15 potential cycles are shown in Fig. 2B (middle curves). N 1s core level peak presents two components. The majority one is again located at 400.1 eV, while the smallest one appears at 403.8 eV. The latter has been assigned to physisorbed N₂ on graphite, thus being a contaminant. [45] The assignment of the former one is a bit more complex. As it has been explained in previous spectrum, binding energy at around 400 eV are usually associated to amine moieties. However, it has also been assigned to benzenoid amine (-NH-) groups appearing upon amino deprotonation and polymerization, which are known to be formed upon electrochemistry.[43, 46–49] On the other hand, the O 1s core level peak remains almost the same as for drop-casted Oxy/GCE, thus indicating that no important variation of the O group has taken place. Therefore, these observations are consistent with Oxy molecules that have polymerized on the GCE surface through the establishment of new intermolecular bonds through amine groups corresponding to a head-to-head interaction. Among the different dimmers reported as possible products of aromatic amines polymerization, head-to-tail, tail-to-tail and head-to-head, the latter agrees with our XPS results.[41]

When the process is repeated using MoS₂/GCE as electrode, an identical result is obtained, with the formation of Oxy polymers *via* the creation of new intermolecular amine bonds. This is evidenced by the presence of the equivalent N 1s and O 1s core level peaks (399.9 and 533.8 eV, respectively, bottom curve). Additionally, a new component appears both in the N 1s and in the O 1s core level peaks at 398.5 (green component) and 531.0 eV (blue component), respectively. The latter corresponds to oxygen in aliphatic compounds, again, probably associated to the solvents used.

3.3 EIS experiments

The Nyquist plots, employing Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ as electrochemical probe, recorded with GCE (curve a), GCE/MoS₂ (curve b) and GCE/MoS₂ after 15 cyclic scans in Oxy solution (curve c) are depicted in Fig. 3. As it can be observed, the semicircle corresponding to the heterogeneous charge-transfer resistance at high frequency values increases from curves a to c. From the data recorded, an increment in the charge-transfer resistance value from 418 Ω to 5100 Ω is obtained for the GCE/MoS₂ system with respect to the bare electrode (GCE). This behaviour, related with a less conductive surface, has been previously reported in the literature and can be explained taking into account that the electrode surface becomes negatively charged as a result of the modification with MoS₂ and, therefore, the Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ system can be repelled. [19] Finally, the Nyquist plot recorded with the GCE/MoS₂ after 15 cyclic scans in Oxy solution shows a huge increase in the charge-transfer resistance until $1.34 \times 10^5 \Omega$. However, far from being a disadvantage, such increase in the charge-transfer resistance supports the benefits of the proposed methodology as the

result confirms that the product of the Oxy oxidation can be electrochemically incorporated onto the MoS₂ surface, allowing a more selective and sensitive quantification.

3.4 AFM experiments

We have characterized the same systems by AFM operating in tapping mode. First, the bare GCE substrate was studied (Fig. 4A). The morphology is characterized by a series of parallel grooves of different widths and depths that are the consequence of the hand polishing process. The rms roughness of the resulting surface is in the 12-13 nm range. In a further step, we also characterized the CGE/Oxy surface (Fig. 4B). Its morphological similarity to that of the GCE electrode surface is evident since the parallel grooves are still clearly visible. Moreover, the rms surface roughness is close to 12 nm. An analysis of the phase contrast image taken simultaneously to the morphological one (Fig. S3) indicates that the contrast is quite homogeneous, which suggests that the GCE coverage by the Oxy is quite homogeneous and not Oxy-free regions are present. Also, the deposition of the Oxy layer should be quite conformal to the GCE surface since the roughness is practically the same, suggesting that the thickness of the Oxy layer is not very large.

Upon incorporation of the MoS₂ structures on the GCE surface, GCE/MoS₂ system, the morphology changes abruptly (Fig. 4C). Now, the surface is mostly covered by flakes of different sizes, ranging from a few nanometers up to the micron scale. In addition, the disposition of these flakes, although it is usually parallel to the underlying substrate, also shows different tilting angles with respect to the x-y plane that can reach values as high as 50° and 70°. The surface has a surface roughness of 77 nm, but the flakes are rather flat since they have a surface roughness close to just 2 nm.

Finally, we have measured (Fig. 4D) the system containing all the components namely, GCE, Oxy and MoS₂, the GCE/MoS₂/Oxy system. The morphology does not differ much from that obtained for the GCE/MoS₂ system as it is mainly defined by the presence of the MoS₂ flakes with sizes up to the micron scale. In this case, the GCE surface is not totally covered by them and the surface roughness is accordingly lower, close to 40 nm. However, a detailed inspection of the grooved regions also reveals the presence of smaller flakes (see inset fig. 4D), with thickness in the 5-15 nm range. In any case, these two features, grooved regions and flakes, lead to quite different phase contrasts (see inset).

3.5 Influence of chemical and instrumental variables

Differential Pulse Voltammetry (DPV) was selected as determination technique in order to reach a highly sensitive Oxy determination. The strategy employed is as follows, i) *electrochemical preconcentration step*: an accumulation potential is applied during a prefixed time, maintaining the GCE/MoS₂ sensor into the analyte solution, in order to produce the adsorption onto the electrode surface of the compound leading to the redox pair at 0.27 V, and ii) *measurement step*: the GCE/MoS₂ electrode is immersed into the supporting electrolyte solution and a DPV scan is recorded between 0.0 and 0.5 V.

In order to obtain the best response of the electrochemical sensor towards Oxy analysis, chemical and instrumental variables were optimized. First, nature and pH of the supporting electrolyte were investigated. To this end, different 0.1 M buffer solutions in the 2-12 pH

range were assayed. These experiments showed an increase in the oxidation current while increasing the pH value up to 5.0. However, higher pH values led to a decrease in the analytical signal (Fig. S4). Therefore, as the highest current intensity was obtained with 0.1 M acetate buffer at pH 5, this medium was selected for further assays.

According to the measurement procedure, the accumulation potential as well as the time during which such potential must be applied are relevant parameters to be optimized. The accumulation potential was studied between 0.50 V and 0.70 V, obtaining the highest signal with 0.60 V. Next, the accumulation time (t_{ac}) was studied at 2 different Oxy concentrations: 5.0×10^{-7} M and 5.0×10^{-6} M. As expected, in both cases the peak current increases with t_{ac} up to a value in which the analytical signal tends to stabilize (see Fig. S5). Such t_{ac} is shorter for the higher Oxy concentration (close to 100 s for 5.0×10^{-6} M), while higher accumulation time is needed when the Oxy concentration is 10 times lower (5.0×10^{-7} M). In this later case, 360 s of accumulation ensures the highest sensitivity.

Finally, pulse amplitude was varied in the 10-80 mV range while scan rate was studied modifying both, the step potential and the interval time. From the results, best conditions (higher oxidation current with low peak width) were obtained with a pulse amplitude value of 60 mV and a scan rate of 10 mV/s.

3.6 Analytical data

Fig. 5 shows the DPV voltammograms, obtained in 0.1 M AcH/Ac⁻ pH 5 as supporting electrolyte, corresponding to the modified electrode after the preconcentration step in solutions with increasing Oxy concentrations.

From the results, a linear increase in the peak current with increasing Oxy concentration was obtained in the 24×10^{-8} M to 1×10^{-6} M concentration range fitting to: $I \text{ (A)} = (1.1 \pm 1.6) \times 10^{-8} + (1.17 \pm 0.03) [\text{Oxy}] \text{ (M)}$ $r = 0.998$. Table 1 summarizes the analytical data calculated in order to evaluate the performance of the proposed methodology. Detection (LD) and determination limits (LQ) were calculated as $3 \sigma/\text{slope}$ and $10 \sigma/\text{slope}$, respectively, where σ corresponds to the standard deviation of the background ($n = 5$) and slope to the calibration slope in the linear range stated above. Moreover, the precision of the method was evaluated in terms of repeatability (successive measurements with the same GCE/MoS₂ electrode) and reproducibility data (measurements with different GCE/MoS₂ electrodes and inter-day measurements). As observed in the table, with the GCE/MoS₂ sensor, Oxy can be detected at 10^{-8} M level with very good accuracy and precision as shown by the corresponding Er % and RDS % values obtained in all the concentration range assayed ($24 \times 10^{-8} - 1 \times 10^{-6}$ M).

Although higher sensitivity can be reached with more expensive and sophisticated techniques as LC-ESI-MS/MS, [37] electrochemical sensors-based methodologies allow the possibility of miniaturization and in situ measurements. As can be seen in Table S1, this methodology allows reaching very good detection and determination limits, better than those reported employing chromatographic techniques and even better than those previously reported with other electrochemical sensors. [35–40]

3.6 Interferences study

In order to study the selectivity of the method, two diamines quite similar to Oxy in structure, 4,4'-diaminodiphenylamine (Ddp) and 4,4'-thiodianiline (Thio), were studied as potential interferences in Oxy determination. To this end, solutions containing a fixed Oxy concentration (5.0×10^{-7} M) mixed with increasing concentrations of the corresponding interference were measured. It was considered that a compound causes interference at a concentration level when it produces a change in the Oxy signal higher than the maximum relative error recorded (8.3%). The presence of Thio together with Oxy leads to a progressive decrease in the Oxy oxidation current that produces interference at 1.3×10^{-7} M Thio level. On the other side, increasing concentrations of Ddp do not produce interference up to 2.0×10^{-6} M, which represents 4-fold concentration level respect to Oxy.

3.7 Analytical application

To test the performance of the method, the sensor was applied to Oxy determination in river water samples. As described in the experimental section, sample aliquots of 4.0 mL (non-spiked and spiked at different Oxy concentration levels in the linear range) were filtered and diluted to 20.0 mL in supporting electrolyte before to be analysed. From the results, no Oxy signal was detected in the unspiked sample but, in the spiked sample aliquots, oxidation current measured at 0.27 V increased with Oxy addition according to $I \text{ (A)} = (-1.3 \pm 0.8) \times 10^{-8} + (1.15 \pm 0.08) [\text{Oxy}] \text{ (M)}$, $r = 0.998$. As observed, the slope obtained with the standard addition method is quite similar to that obtained with the external calibration ($1.17 \pm 0.03 \text{ A} \times \text{M}^{-1}$), suggesting that no matrix interference is produced in these conditions. To confirm this statement, t student statistical comparison was performed. As lower t_{cal} value (0.408) than $t_{\text{tab}(95\%)}$ (2.776) was obtained, it can be concluded that no significant differences exist between the slopes, supporting the hypothesis that no matrix interference is produced. Therefore, the recovery of the proposed methodology was evaluated over spiked samples by direct interpolation in the external calibration curve. Samples were analysed in triplicate and the results are summarized in Table 2. The good recoveries obtained allow us to conclude that the CGE/MoS₂ sensor can be satisfactory applied to Oxy determination in river samples with no sample treatment but a simple filtration.

4 Conclusions

This work shows that MoS₂ nanosheets are excellent nanomaterials in the design of an electrochemical sensor towards Oxy analysis, since they allow diamine preconcentration on the electrode surface previously to its electroanalytical determination.

After the preconcentration step, XPS results confirm the presence of Oxy-related structures on the surface of the electrode and suggest the formation of an Oxy polymer via the establishment of new intermolecular bonds between amine groups, leading to hydrazobenzene. Moreover, AFM results show a morphology characterized by the presence of rather flat MoS₂ flakes of sizes ranging from nano to microscale covered by an Oxy layer.

The detection of Oxy through the peak ascribed to the hydrazobenzene formed in the preconcentration step, which appears at low potential values, allows diminishing

interferences produced by compounds that can be present in the sample. Moreover, our sensor allows Oxy determination with excellent detection limits, accuracy and precision, without need to include other nanomaterial in the sensor construction together with MoS₂, in contrast to most of the procedures reported involving TMDs for electrochemical sensor development. Then, MoS₂ can be used to improve the analytical response towards this kind of contaminants and even to eliminate them from wastewaters since the diamine compound can be separated from the sample in an extraction-like step.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.

A) Cyclic voltammograms recorded with a GCE/MoS₂ electrode in 0.1 M AcH/Ac⁻ pH 5 as supporting electrolyte in the absence (a) and in the presence (five successive scans, b-f) of 0.1 mM Oxy solution. B) Cyclic voltammograms recorded with a GCE/MoS₂ electrode in 0.1 M AcH/Ac⁻ pH 5 before (a) and after (b) 5 consecutive scans in 0.1 mM Oxy solution. Inset: Current intensity at $E_p = 0.27$ V versus successive cyclic voltammetric scans at a GCE/MoS₂ and at a GCE electrodes in Oxy solution. Scan rate = 100 mV/s

Fig. 2.
XPS analysis of the samples. A) Schematic representation of the Oxy molecule. B) N 1s core level peak of three different samples. C) O 1s core level peak of the three samples in panel B).

Fig. 3. Nyquist plot of 10.0 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1 M phosphate buffer pH 7 obtained with a) GCE; b) GCE/ MoS_2 and c) GCE/ MoS_2 after 15 cyclic scans in 0.1 mM Oxy solution. Inset: Zoom of high frequency area.

Fig. 4. AFM characterization of the different electrode surfaces. A) GCE. B) CGE/Oxy. C) GCE/MoS₂. D) GCE/MoS₂/Oxy. Inset: Phase-contrast image taken simultaneously with D.

Fig. 5. DPV voltammograms recorded with the GCE/MoS₂ electrode when increasing the Oxy concentration in solution during the preconcentration step. Inset: Calibration graph. Conditions: accumulation time=360s, pulse amplitude=60 mV, scan rate=10 mV/s.

Table 1

Analytical data obtained for a GCE/MoS₂ sensor towards Oxy determination. RSD* repeatability data. RSD** reproducibility data.

Sensitivity A×M ⁻¹	LD (M)	LQ (M)	Er (%)	RSD* (%) _{n=5}	RSD** (%) _{n=5}
(1.17 ± 0.03)	8×10 ⁻⁸	24×10 ⁻⁸	<8.3	<5.1	<5.6

Table 2

Recoveries obtained from the analysis of Oxy in river water spiked samples with the GCE/MoS₂ sensor.

Oxy added (μM)	Oxy found (μM)	Recovery %(n=3)
0.31	0.29	94
0.49	0.46	94
0.69	0.66	96