An ultrasensitive and highly selective nanomolar electrochemical sensor based on an electrocatalytic Peak Shift Analysis approach for copper trace detection in water.

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Abstract :

Copper (Cu) sensing in the nanomolar range is an important challenge for marine water monitoring, especially with eco-friendly materials and reagents. For this purpose, electrochemical Cu(II) sensors appear as fully suitable because of their relatively high sensitivity, selectivity and adaptability for in situ measurements. So far, one of the usual electrochemical methods for Cu(II) sensing is adsorptive anodic stripping voltammetry (AdASV), since it offers a good selectivity, accumulation at open circuit potential and a reliable analytical response for concentrations above 10 nmol.L−1. Surprisingly, no work has ever addressed an electrocatalytic procedure to enhance the electrochemical copper sensing and allowed detection below 10 nM. Thus, we have developed an original two-step strategy based on the surface modification of pencil graphite electrodes (PGE) with p-aminobenzyl-C-functionalized cyclam, a strong chelating ligand for Cu(II), as well as the use of a simple reaction which can be electrocatalyzed by Cu such as HER (Hydrogen Evolution Reaction) to finally determine the accumulated amount of copper catalyst on the PGE. We show here that i) a well-defined diffusion-limited catalytic peak can be obtained from cyclic voltammetry (CV) experiments with Cu(II)-cyclam-modified PGE, ii) this HER peak potential is correlated to copper surface concentration, which can be sensed at the same time by adsorptive anodic stripping voltammetry and iii) peak shift analysis (SA) of the voltammetric curves is a more sensitive method than the commonly used stripping voltammetry to reveal copper accumulation at modified PGE. Indeed, the limit of detection (LOD) reached with this method is one order of magnitude lower compared to AdASV (LOD = 1.1 nM and 16 nM, respectively). These results illustrate the ability of electrocatalysis to be a relevant tool under certain conditions for metal trace detection through SA.

Highlights

► Modified pencil graphite electrodes with p-aminobenzyl-C-functionalized cyclam can be used for the passive accumulation of copper ions at open circuit potential. ► Nanomolar amounts of copper can be determined by using both stripping and catalytic electrochemical approaches with copper cyclam-modified

graphite electrodes. ► Peak shift analysis of the electrocatalytic HER voltammetric curves allows accurate quantification of copper concentration in the nanomolar range with a higher sensitivity compared to adsorptive stripping voltammetry. ► Electrocatalytic proton reduction is highly dependent on electrolyte composition.

1. Introduction

Copper (Cu) is an essential micronutrient for the marine environment since it is involved in many oceanic biochemical processes [1-3]. However, copper also plays a dual role as a poison in affecting the metabolism of biological organisms [4-5] and the toxic concentration of copper depends on the considered biological species. For example, the acute toxicity of copper was evaluated to be equal to 9.5 μmol.L^{-1} for green crab, 92 nmol.L^{-1} for blue mullet, [6] whereas for some microalgae, the lethal concentration of copper is close to the optimal content for their own growth [7]. Moreover, copper toxicity is strongly related to its available form, i.e if copper is included in the particulate fraction (particles size > 0.45 μm) or in the dissolved one (particles size < 0.45 μm). The latter, being considered as the more harmful, includes free Cu^{2+} (0.2%) but is mainly constituted (99.8%) of complexes resulting from Cu(II) chelation by natural ligands (humic substances). As a landmark, recent works have reported low concentrations of total dissolved copper in rivers, estuaries and coastal oceans (3 to 4 nmol.kg^{-1}) [8] but these concentrations are increasing due to human industrialization [9] reaching tens of nanomolar [10] in estuaries. Thus, total dissolved Cu(II) concentration must be sensed in the nanomolar range, and free copper in the picomolar one, to monitor local toxic events affecting biological activities.

For this purpose, electrochemical methods, such as the well-known anodic stripping voltammetry (ASV), have been intensively used [11-12]. These methods have even been applied *in situ* for copper analysis in the marine environment with the voltammetric *in situ* profiling technique (VIP) [13-14] or more recently with the

ElViDor device [15]. These instruments can achieve limit of detection (LOD) values in the nanomolar range. However, due to the high toxicity of mercury and in agreement with the 2008/105/EC and 2011/65/UE European guidelines, the mercury layer used in the VIP needs to be replaced. Moreover, the resolution for the ElViDor system can be negatively impacted by peak overlapping of other electroactive non-metallic species. To address these issues, electrode surface modification for sensing purposes can be a relevant strategy, since it selectively pre-concentrates a metal of interest [16-19]. In that field, cyclam (1,4,8,11-Tetraazacyclotetradecane) has been recognized as an excellent ligand for copper detection by adsorptive anodic stripping voltammetry (AdASV) [20-26]. Different processes of surface functionalization [20-21],[23-25] on various electrode types [20-21],[23-24] have been reported, leading to various cyclam surface densities and consequently to diverse analytical performances. On one hand, a drop casting method demonstrated the highest cyclam coverage associated with the largest linear range for copper detection (3 orders of magnitude) starting at 1 nmol.L^{-1} [24]. However, due to the presence of an inhomogeneous and disorganized receptor layer [27-28], this sensor is also the less selective one against iron, nickel and zinc. On the other hand, cyclam-based sensing layers obtained with surface modification by silane chemistry [20] and electroreduction of diazonium salts [21] displayed better selectivity for copper sensing. However, due to the low surface concentration of cyclam, the limit of quantification (LOQ) was one order of magnitude higher compared to drop casting process. Finally, using a high surface to volume ratio electrode such as graphite felt [23] was shown to be helpful for decreasing Cu(II) LOQ. So far, in these reported works, only *N*-functionalized cyclams were used as

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bifunctional chelators, while it has been demonstrated that this way of modification is deleterious for copper chelation selectivity compared to a *C*-functionalized one [29]. Moreover, despite their excellent conductivity, low capacitive current, good reproducibility, adjustable surface area and very low cost, pencil graphite electrodes have never been used for these applications.

In the meantime, many copper complexes [30] have been developed for sustainable energy production, generating dihydrogen and dioxygen through Hydrogen and Oxygen Evolution Reaction (HER [31-36] and OER [37-42]) in homogeneous [31-37] or heterogeneous [32-42] ways. For the latter, many copper complexes have been reported to serve as precursors for copper-based nanomaterial electrodeposition, leading to electroactive films with excellent catalytic efficiency. Nevertheless, and to the best of our knowledge, these catalytic activities have never been exploited for the development of copper detection. Sensors based on electrocatalysis are principally used to directly measure substrate concentration in solution [43], the catalytic reaction allowing significant enhancement of the electrochemical signal [44]. In those cases, current intensities are exclusively converted to substrate concentration.

In this work, we propose to explore a different kind of electrochemical sensors, based on heterogeneous electrocatalysis, where the targeted species to analyse is the catalyst (Cu) and no longer the substrate. Indeed, under certain conditions ("total catalysis", see below) and according to theoretical works for electrocatalysis at a modified electrode [45], the potential of the catalytic peak obtained by CV can vary with the surface concentration of the catalyst, as described by equation (1) for a Nernstian (fast and reversible electron transfer) case:

$$E_{\text{cat}}^{0,\text{ap}} = E_{\text{P/Q}}^0 + \frac{RT}{nF} ln\left(\frac{k\Gamma_{\text{P/Q}}^0}{\sqrt{\frac{D_s nFv}{RT}}}\right) \quad (1)$$

with $E_{\text{cat}}^{0,\text{ap}}$ being the apparent standard catalytic potential, $E_{\text{P/Q}}^0$ the standard potential of the P/Q couple, $\Gamma_{\text{P/Q}}^0$ the surface concentration of the catalyst, D_s the diffusion coefficient of the substrate, k the rate constant of the catalytic reaction and v the scan rate.

The equation (1) is valid for the well-known "total catalysis" case, for which the rate of the catalytic reaction is so fast that the catalytic reaction is controlled by the diffusion of the substrate. According to this equation, it may be possible to directly determine the surface concentration of the catalyst by simply measuring the value of the potential ascribed to the catalytic peak. Thus, the namely peak shift analysis (SA) may be considered as a new way to report copper surface concentration. For that purpose, we used cyclam under its C-functionalized version by a para-aminobenzyl pendant (p-H$_2$N-Bn-cyclam). This ligand was first covalently immobilized onto PGE by a diazonium approach (see experimental section for details). In a second step, the modified PGE was dipped in a solution of copper. Finally, the Cu-modified electrode was studied in a copper-free solution thanks to AdASV and SA approaches (Fig. 1). To validate this strategy, we have initially optimized the experimental conditions (supporting electrolyte, pH) and performed comparative studies with PGE surfaces modified with copper layer but without cyclam. From the resulting experiments, we have then explored the sensing properties of our modified cyclam PGE system in the frame of the HER reaction leading to significant enhancement of the LOD compared to the classic stripping methods. This work thus paves the way for a new eco-friendly

strategy for highly sensitive detection of pre-concentrated metals at modified electrode.
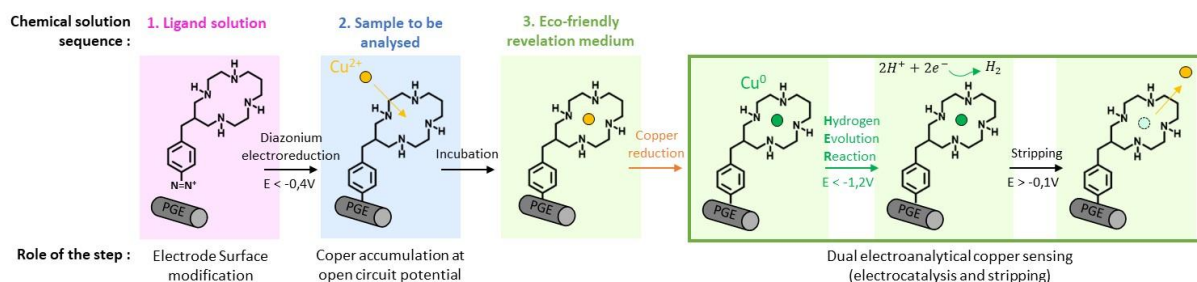

Fig. 1. Schematic diagram of the experimental principle envisioned in this work.

2. EXPERIMENTAL

2.1. Chemicals and reagents

In order to avoid any copper contamination, reagent preparation was performed according to trace metal clean techniques using high quality products. Sulfuric acid (95-97%), sodium chloride (99.99%), potassium chloride (99.999%) were purchased from Merck. Sodium nitrite (99.999%), calcium chloride dihydrate (> 99%), perchloric acid (70%) and ruthenium(III) hexamine trischloride [Ru(NH$_3$)$_6$]Cl$_3$) were purchased from Sigma Aldrich. Magnesium chloride hexahydrate, sodium sulphate anhydrous NORMAPUR and ethanol 96% were purchased from VWR. Sodium perchlorate was acquired from Alfa Aesar, ortho-phosphoric acid 85% and mono-sodium phosphate were purchased from Fluka. *p*-H$_2$N-Bn-cyclam was synthesized as previously described [46]. All solutions were prepared with purified water (18.2 MΩ.cm, pH = 6.3) from a Milli-Q system (Millipore). Prior to any use, solutions were deoxygenated by bubbling nitrogen for 5 min. To avoid metal contamination, electrochemical cells were rinsed

firstly with 10 % of HCl solution and then with Milli-Q water before use. Pencil leads (Pilot ENO-G 0.3mm HB) were commercially purchased.

2.2 Electrode preparation

PGE surfaces were first examined by scanning electron microscopy (SEM). SEM images (Fig. SI.1) show µm-sized longitudinal grooves which were probably formed during the industrial production process. PGE were produced from a 6 cm pencil lead (0.3 mm in diameter) cut into 2 cm rods with a scalpel blade, sonicated for 5 min in 96 % ethanol solution, rinsed 3 times in ethanol 96 % and dried at 70 °C during 15 min. To avoid any metal contamination from the electrode surface, the electronic link between the potentiostat and PGE was ensured thanks to a homemade disposable connection with a 0.7 mm diameter pencil graphite rod and a small piece of silicon sleeve. To ensure reproducible and comparable measurements between all experiments, a strict protocol was defined to mount the electrochemical cell: the same glass cell and its lit in Teflon (Palmsens) was systematically used, and the glass cell was filled by 5 ml of solution. Each electrode (Reference (RE), counter (CE) and working (WE)) had its defined location through the lit and in the cell, so their relative positions never changed. By this way, inter-electrodes distances and surface exposed to the solvent were constant. Finally, only 1 cm of the PGE and 2 cm of the platinum counter electrode were dipped in the studied solution (working geometric area $S_{geo,WE}$ = 0.095 cm² and $S_{geo,CE}$ = 0.315 cm²). For PGE, voltammograms obtained in H_2O/KCl 0.1 Mol.L^{-1} with [Ru(NH$_3$)$_6$]Cl$_3$ (1 10^{-3} Mol.L^{-1}) at pH 6 allowed to calculate the electrochemical area $S_{elec,WE}$ = 0.097 ± 0.004 cm² (considering $D_{Ru(NH3)6}$ = 5.3x10^{-6} cm².s^{-1}), i.e a roughness factor equal to 1.03.

2.3 Electrochemical measurements

All electrochemical measurements were performed with a Bio-logic potentiostat (VSP), using a conventional three electrodes system, comprising a platinum counter electrode (0.5 mm in diameter), a silver/silver chloride reference electrode (Ag/AgCl/saturated KCl) and a pencil-graphite working electrode.

2.4 Electrochemical PGE modification with *p*-H$_2$N-Bn-cyclam

Electrodes were modified by electrochemical reduction of *in situ* generated diazonium salt according to a reported procedure [46]. To generate the diazonium salt, 1 mg.mL^{-1} solution of *p*-H$_2$N-Bn-cyclam was added to a solution of NaNO$_2$ (1.1 eq.) in 0.01 mol.L^{-1} H$_2$SO$_4$. The lifetime of the diazonium species was monitored thanks to its reactivity with N-(1-naphtyl)-ethylenediamine as already published [47] (Fig. SI.2). PGE were functionalized by applying a fixed potential (E = −0.7 V vs. Ag/AgCl) until a total charge of 50 μC was passed through the circuit (Fig. SI.3). Considering the cylindric shape of the WE and the electrochemical cell configuration, the electric field distribution toward the WE led to the *p*-H$_2$N-Bn-cyclam electrografting mainly over the WE side facing the other electrodes. Each modified PGE was used a single time.

2.5 Preparation of PGE electroplated with copper

Copper electroplating on PGE was performed by chronocoulometry, applying of a reductive potential of −0.8 V vs. Ag/AgCl in a solution of 1.10^{-3} mol.L^{-1} CuSO$_4$ / 1 mol.L^{-1} H$_2$SO$_4$. Depending on the desired copper amount, various deposition times were applied.

2.6 Analytical procedure for Cu(II) measurements

Copper sulfate solutions (1-1000 nmol.L^{-1}) were used as model solutions to explore the SA method using cyclam-modified PGE. Considering this new methodology for an eco-friendly marine use, artificial seawater (450 mmol.L^{-1} NaCl, 10 mmol.L^{-1} KCl, 9 mmol.L^{-1} CaCl$_2$, 30 mmol.L^{-1} MgCl$_2$, 16 mmol.L^{-1} MgSO$_4$, pH = 7.8 adjusted with NaOH) [48] was spiked with known amounts of Cu^{2+} in the nanomolar range, to demonstrate the feasibility of the measurement in natural sample . The electrodes were dipped 30 minutes in copper solution to ensure that the thermodynamic equilibrium between chelated and free copper was reached. After incubation, electrodes were rinsed with Milli-Q water. Voltamperometric measurements were performed at various pH values and for various supporting electrolytes by soaking the modified electrodes in different electrolytic solutions. Considering all of these steps, and including PGE mounting, less than 60 min were required to measure copper concentration.

3. RESULTS ANS DISCUSSION

3.1 Investigation of the catalytic proton reduction by Cu-cyclam-modified electrodes

Our first objective was to demonstrate that cyclam-modified PGEs could effectively trap Cu^{2+} ions for further sensing by electrochemical methods. For that purpose, cyclam-modified PGE were soaked in a 1 µmol.L^{-1} concentrated Cu^{2+} solution [20-25], rinsed with Milli-Q water and studied by CV in sodium perchlorate at pH = 3 [22]. During CV, when the WE reached the cathodic potential of −0.6 V, the resulting voltammogram revealed an anodic peak ascribed to Cu(0) dissolution on the back

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scan (Fig. SI.4). Unless the cathodic limit reached −0.6 V, no dissolution signal was recorded. The potential of this oxidation peak was found to vary between −0.075 and −0.015 V vs. Ag/AgCl. As the cathodic limits was pushed towards more negative values, the Cu(0) oxidative peak intensity increased, reaching a maximal faradic current of 0.72 ± 0.05 µA for a cathodic limit at −1.0 V. From this result, the maximal quantity of copper chelated at the electrode was evaluated from the area of the oxidation peak. A value of 12.5 ± 0.9 µC.cm^{-2} was found, meaning that a maximum of 65 ± 5 pmol.cm^{-2} of cupric ion could be trapped.

Knowing that copper uptake was possible with the cyclam-modified PGE, the next goal was then to evaluate how equation (1) could be relevant to measure copper amounts in a sensing perspective. For this purpose, experimental conditions for obtaining a well-defined and reproducible heterogeneous copper induced electrocatalytic signal were explored. Considering the abundant literature on copper complexes for the production of dihydrogen, we first investigated the possibility to perform proton reduction at cyclam-modified PGE with chelated copper.

For this, CV experiments were performed in various electrolytes ($CH_3CO_2NH_4$, $NaClO_4$, Na_2SO_4, NaH_2PO_4) and for various pH values (7, 6, 5, 4 and 3), starting from the open circuit potential (E_{oc}) to strong cathodic potential to explore HER, followed by a reversed scan to reveal copper re-oxidation (Fig. 2. and Fig. 3). Acetate and perchlorate-based electrolytes were first chosen because the former was systematically used in previous papers describing copper detection by cyclam-modified electrodes [20-25], whereas the latter has the advantage to be weakly coordinating, unlike acetate, and also to be redox-innocent [49]. For these

experiments, the cylam-modified PGE were pre-dipped in a Cu^{2+} solution (100 nmol.L$^-$^{1}), then rinsed with water and studied in a copper-free electrolytic solution.

As shown in Fig. 2A, CVs performed in ammonium acetate led to the appearance of an intense cathodic wave (onset at -1.1 V) upon negative scan, while a much less anodic peak corresponding to Cu(0) oxidation was detected at -0.1 V when scanning positively. The current for the cathodic peak was found to strongly increase inversely to the pH, in strong contrast to anodic peak which remained constant for 3 < pH < 6 (inset Fig. 2A). Bubble formation was observed from -1.3 V as expected for HER. Interestingly, when using sodium perchlorate, current densities for the reduction process were significantly lower than for acetate (Fig. 2B). Moreover, a peak current instead of a wave was observed for pH < 5 ($E_{pc} = -1.20$ V at pH = 4 and -1.45 V at pH = 3, see Fig. 2B, blue and pink curves). However, changing the supporting electrolyte did not modify the anodic signature. For cyclam-modified PGE which were not soaked in any copper(II) solution, no cathodic peak current could be observed for this potential range (Fig. 4A, red curve). These results thus i) show that copper accumulated by the ligand is involved in a reduction process that depends on pH, indicating HER and ii) confirm the results obtained by Siewert et $al.$[50], who demonstrated that the counter anion used in the electrolyte may strongly interfere during HER.
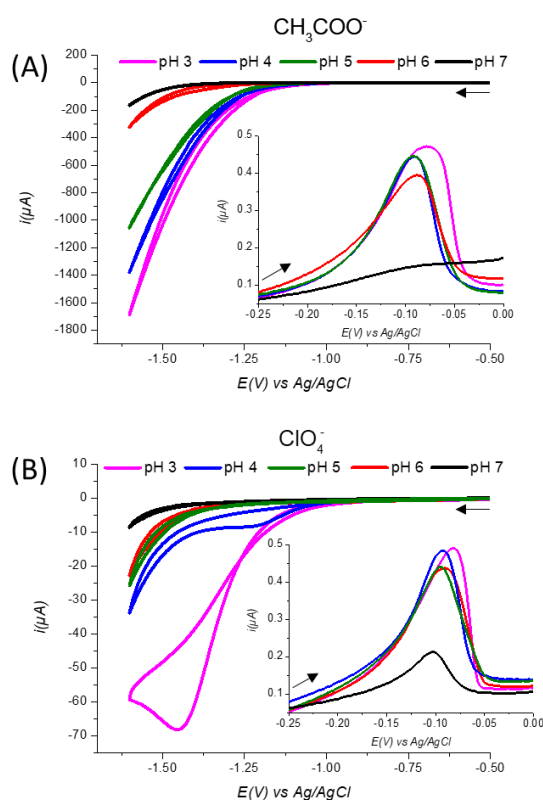
Fig. 2. Cyclic voltammograms recorded at 50 mV.s^{-1} at pH = 3, 4, 5, 6 and 7 in ammonium acetate (A) and NaClO$_4$ (B) Inset: enlargement of the copper stripping potential window.

In order to confirm this hypothesis, three supplementary sodium-based supporting electrolytes (acetate, sulfate and phosphate) were investigated at pH = 3. As shown in Fig. 3, the anion of the electrolyte has a significant influence on the cathodic electrochemical signal, but minor effect on copper(0) oxidation. Considering acetate (Fig. 3, black curve) and phosphate (red curve), an important reduction current appeared at −1.0 V and −1.2 V respectively, decreasing almost linearly, without showing a well-defined electrochemical peak, in contrast to perchlorate (pink curve) and sulfate anions (blue curve). For the latter, a sharp catalytic electrochemical signal

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was observed at −1.37 V, close to the catalytic potential obtained for perchlorate but with a peak intensity 2.5 times higher.

For the anodic signal (Fig. SI.5), the copper quantities that were oxidized were very close for sulfate and perchlorate anions (202 and 208 nC, respectively). Slightly lower charges quantities were measured for phosphate and acetate electrolytes (186 and 142 nC). According to these results, best conditions for Cu(II) detection by CV were obtained with Na_2SO_4 (0.1 mol.L^{-1}) at pH = 3.
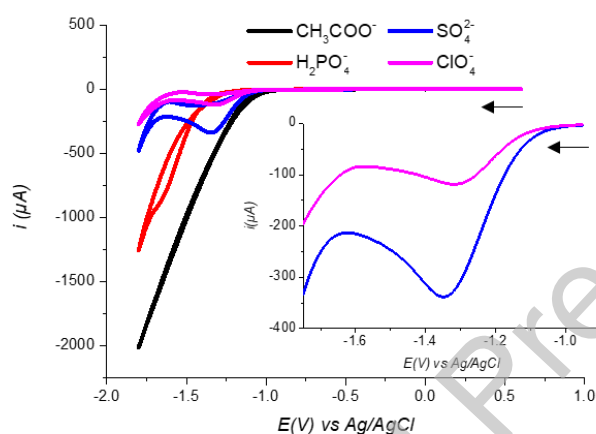

Fig. 3. Cyclic voltammogram recorded at 50 mV.s^{-1} of PGE/cyclam/Cu(II) in different electrolytes (0.1 mol.L^{-1}) at pH = 3 in acetic acid / sodium acetate, sodium phosphate / phosphoric acid, sodium sulphate / sulfuric acid and lithium perchlorate / perchloric acid. Inset: enlargement of the forward cycle for sulphate and perchlorate counter anions as the electrolyte.

As the counter anion seemed to play a significant role during the reduction reaction, and considering the SO_4^{2-}/SO_2 couple (E^0 = 0.16 V vs. NHE), we hypothesized that sulfate ion could be involved as a co-factor into the HER catalytic process or may be a

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part of the faradic yield. For this purpose, the catalytic peak obtained with a Cu-cyclam-modified PGE was first analysed from CVs at different pH values in sulfate medium. A current variation of -151 ± 4 mA.$[H^+]^{-1}$ as well as a potential shift of 92 ± 1 mV/pH were found. Since the expected shift for a Nernstian (fast) reaction involving n electrons and m protons is (m/n)59 mV/pH, the latter value may indicate that the redox reaction implies n=m proton and electron, but is kinetically limited, biasing the experimental measurement of the m/n ratio [51-52]. By increasing sulfate concentration at pH = 3, current values showed a linear variation with the sulfate concentration with a slope of -0.221 ± 0.001 mA.$[SO_4^{2-}]^{-1}$, i.e. 3 orders of magnitude lower than the case of proton (-151 mA.$[H^+]^{-1}$). Thus, considering the high consumption of proton at the vicinity of the electrode producing H_2 and the need of proton for sulfate reduction, it is reasonable to propose that sulfate acts preferably as a co-substrate during HER rather than being reduced into SO_2. This hypothesis was verified by using perchlorates instead of sulfates, or with bare PGE instead of Cu-cyclam-modified PGE. Results obtained showed that (i) sodium sulfate as electrolyte increases proton reduction efficiency compared to sodium perchlorate (3-fold increase), (ii) the current variation measured in sulfates at different pH values with Cu-cyclam-modified PGE is close to that measured with bare PGE (iii) increasing perchlorate concentration at pH = 3 does not increase the catalytic intensities during HER unlike sulfate and (iv) sulfates have less effect on the HER catalytic current on bare PGE compared to Cu-cyclam-modified electrodes. These results are thus in favour of a specific process implying copper, sulfate and protons, with a faradic yield exclusively attributed to H_2 production.

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Further studies were then carried out to rationalize the impact of the electrode material on the electrochemical sensing, since it is well-known that the HER overpotential is fully material-dependent [53]. Four different PGE (bare, cyclam-modified, Cu-electroplated and Cu-dipped modified-cyclam) were tested in Na_2SO_4 0.1 mol.L^{-1} at pH = 3. The Fig. 4 displays the CV responses for proton reduction (cathodic peak) and Cu dissolution (anodic peak).
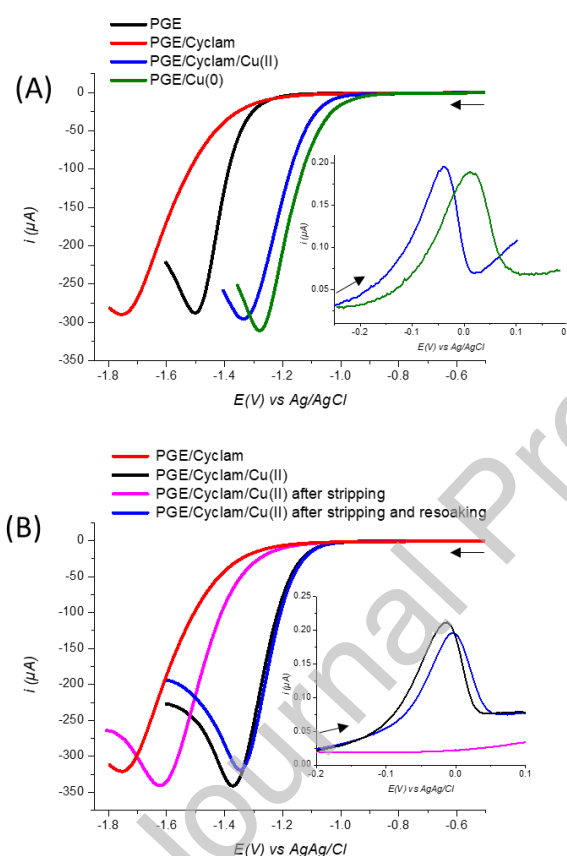

Fig. 4. (A) Forward scan of the cyclic voltammograms of PGE, copper electroplated PGE, cyclam/PGE and PGE/cyclam/Cu(II), in Na_2SO_4 pH = 2,7 at v = 50 mV.s^{-1}. (B) Evolution of the catalytic peak potential depending on the re-use of the modified electrode. Insets: enlargement of the oxidation signal of copper.

As shown in Fig. 4A, the catalytic peak height intensities reached 300 µA whatever the electrode interface. This observation is consistent with a substrate-diffusion controlled catalytic process ("total catalysis"). In strong contrast, the peak potential was highly material-dependent, varying from −1.70 (for PGE/cyclam) to −1.32 V (for PGE/Cu(0)). Here, the shift in peak potential may be ascribed to the catalytic rate, which is likely the highest for PGE/Cu(0) and PGE/cyclam/Cu(II). The Cu-free cyclam-modified PGE (Fig. 4A, red curve) displayed a more negative and broader peak than the bare PGE (Fig. 4A, black curve), as probably resulting from an insulating effect due to the organic cyclam layer. The slight difference in potential between cyclam-modified electrode with copper (Fig. 4A, blue curve, E = −1.34 V) and copper electroplated electrode (green curve, E = −1.28 V) may arise from the difference of copper amount onto the electrode surface, determined at 252 and 304 nC from the oxidation peak (inset Fig. 4A), respectively. To ensure that the HER electrochemical signal obtained with Cu-cyclam-modified PGE was not related to the release of free copper from ligand decomposition [50], a simple test was carried out consisting in re-using the PGE after electrochemical demetallation at 0.0 V and re-metallation with Cu^{2+}. As shown in Fig. 4B (pink curve), the catalytic peak after stripping was shifted negatively, and approached the value found for the cyclam-modified PGE (Fig. 4B, red curve). Dipping the unmetallated electrode into a copper(II) solution led to the full recovering of the catalytic signal at closed potential (Fig. 4B, blue curve *vs.* black curve) accompanied by a stripping signal equivalent to the previous one (206 nC and 216 nC, respectively). These results show that even after being used for HER and copper stripping, cyclam moieties at the electrode maintain their complexing

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properties, since both cathodic signal during HER and anodic signal during copper stripping were recovered. Thus, the cathodic signal does not seem associated with a decomposition of the cyclam ligand.

3.2 Comparative determination of nanomolar copper(II) concentration by AdASV and SA approaches.

After evidencing that the HER catalytic signal was optimized in sodium sulfate at pH = 3, we explored the possibility to exploit the peak potential shift to precisely determine $[Cu^{2+}]$ in the solution, i.e the SA approaches. For this purpose, cyclam-modified PGE were dipped in Cu^{2+} solution of variable concentration (ranging from 1 to 150 nM). After incubation, the electrodes were rinsed with ultrapure water and placed in a solution of Na_2SO_4 0.1 $mol.L^{-1}$ at pH = 3 for voltamperommetric measurements.

Anodic stripping voltammetry was first used to correlate copper surface concentration to solution concentration. Well-defined anodic peaks (Fig. SI.6a) were detected at $E > -0.125$ V for $[Cu^{2+}] > 10$ $nmol.L^{-1}$. The peak integration (Fig. SI.6b) allowed us to determine the copper LOD at 16 $nmol.L^{-1}$ (3σ method) in accordance with Walcarius [20] *et al.* (LOD = 10 $nmol.L^{-1}$) and Jasmin [21] *et al.* (LOD = 13 $nmol.L^{-1}$). For lower Cu^{2+} concentration, no significative peak could be obtained by cyclic voltammetry, because of the decrease of the signal to noise ratio (S/N).

Since copper concentration can be calculated from the anodic peak integration, the copper quantities accumulated at E_{oc} were plotted against the corresponding copper concentration in solution. Results were fitted with both Langmuir (equation (2)) and Hill isotherms (equation (3)):

$$\frac{\Gamma_{Cu^{2+}}}{\Gamma_{Cu^{2+},max}} = \frac{K_{a,surf}[Cu^{2+}]}{1+K_{a,surf}[Cu^{2+}]} \qquad (2)$$

$$\frac{\Gamma_{Cu^{2+}}}{\Gamma_{Cu^{2+},max}} = \frac{(K_{a,surf}[Cu^{2+}])^q}{1+(K_{a,surf}[Cu^{2+}])^q} \qquad (3)$$

where $\Gamma_{Cu^{2+}}$ is the surface concentration in Cu(II) (mol.cm^{-2}), $\Gamma_{Cu^{2+},max}$ is the maximum surface concentration, $K_{a,surf}$ the association constant characterizing the copper - cyclam complex at the electrode surface and q is a cooperative coefficient [54]. According to these nonlinear fittings, Hill isotherm offers the best results (adjr² = 0.99836 vs. 0.99502 for Langmuir, (Fig. SI.6c) with a maximal surface concentration estimated at 97 ± 5 pmol.cm^{-2}. The latter is similar to that found from peak integration after dipping in a 1 µmol.L^{-1} copper solution (65 ± 5 pmol.cm^{-2}). Accordingly, the value of $K_{a,surf}$ was found to be very low compared to the association constant $K_{a,sol}$ reported in solution. Indeed, log $K_{a,surf}$ was estimated at 6.24 ± 0.05, while log $K_{a,sol}$ = 26.50 [12]. This difference may originate because it is well known that after immobilization, a receptor displays lower affinities for the targeted species mainly because of steric hindrance or vicinity interactions [52-55]. Finally, it is very interesting to note that since Hill coefficient is superior to one (q = 1.255 ± 0.049), positive cooperation between the binding sites seems to occur during the accumulation [56].

The voltammetric data were then analysed through the SA approach. As shown in Fig. 5A, a positive shift of the peak potential was detected when the copper concentration in solution was increased from 0 to 175 nmol.L^{-1}. Analysis of these data (Fig. 5B) showed two trends according to copper concentration. A pseudo-linear variation of

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the peak potential was found for $[Cu^{2+}]$ ranging between 0 and 10 nmol.L^{-1}, with a slope of 0.020 ± 0.001 V/$[Cu^{2+}]$ (r=0.9825). The LOD calculated with the 3σ method reached a remarkable value of 1.1 nmol.L^{-1}, which is more than one order of magnitude lower compared to the AdASV method (16 nmol.L^{-1}). For higher copper concentration (10 nM < $[Cu^{2+}]$ < 175 nM), the peak potential also shifted towards more positive values but asymptotically reached a steady value at −1.33 V from $[Cu^{2+}]$ = 100 nM. Further analysis was carried out by plotting the cathodic peak potential against surface concentration. Since surface concentration below 10 nM could not be achieved from ASV, we used the Hill isotherm (equation (3)) to evaluate it for $[Cu^{2+}]$ < 10 nM. A slope of 62.9 mV / $\ln(\Gamma^0_{Cu^{2+}})$ was obtained by the non-linear regression (Fig. SI.7). This value is higher than that expected (12.6 mV / $\ln(\Gamma^0_{Cu^{2+}})$) for a classical "total catalysis" case (equation (1)), and may result from interference of the heterogeneous electron transfer in the kinetics of the whole process [45].
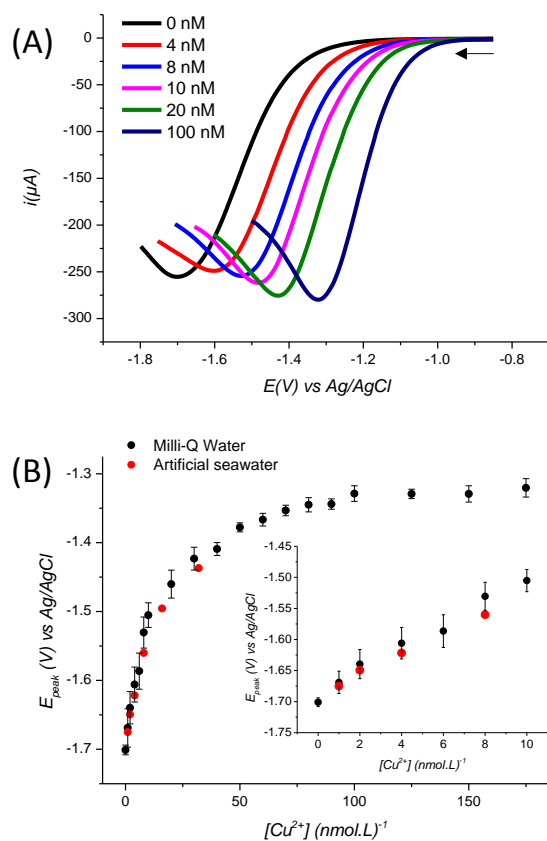
Fig. 5. (A) Forward scan of the catalytic peaks measured after incubation of PGE/Cyclam in solution containing increasing Cu^{2+} concentrations (0 (black), 4 (red), 8 (blue), 10 (pink), 20 (green), 100 (dark blue) $nmol.L^{-1}$) (B) Potential evolution of the catalytic peak represented in A: E_{peak} (V) = f([Cu^{2+}]).

In order to fully evaluate our cyclam-based system, comparative studies were then performed with PGE electroplated with various amounts of copper (no cyclam). Indeed, we wanted to evaluate an "ASV-like" protocol where the electroplated copper is first used as a catalyst for HER before being stripped. For this objective, different amounts of copper were electroplated onto PGE by chronocoulometry, and CVs in Na_2SO_4 at pH = 3 were performed, starting at E_{oc} towards −1.8 V (revealing

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copper through HER) and then reversing until 0.5 V (revealing copper by its oxidation). As the amount of electrodeposited copper was increased, the catalytic peak shifted towards more positive potential, as expected (Fig. SI.8). However, since HER occurred on bare PGE near -1.4 V (Fig. 3), the method was found to be unsuitable for low quantities of copper because of the interference of the HER catalysed by carbon. By this way, we measured that a minimal quantity of copper of 8 pmol.cm^{-2} was necessary to produce a detectable signal by SA, while the stripping method could allow lower Cu(II) detection. In other words, ASV appeared as a more sensitive method than SA during HER with the Cu-electroplated electrode. This result emphasizes that for SA measurements, the support material needs to be well controlled not to interfere into the catalytic signal. In order to have a full comparison between cyclam-modified and non-modified electrodes, values of peak potential were plotted against copper surface concentration (Fig. 6). It can be observed that the LOD in SA methods is limited by the electrocatalytic properties of the material, while for ASV the LOD is imposed by the S/N ratio. Moreover, since the limit of linearity of the SA method (LOL $\approx$ 10 nM) proposed in this work corresponds to the LOD in AdASV (LOD = 16 nmol.L^{-1}), it is interesting to note that performing AdASV in Na$_2$SO$_4$ at pH = 3, SA can be a complementary method to the conventional stripping analysis, confirming copper amount at the electrode surface, or helping to interpret ambiguous oxidation signal. Together, these two approaches allow detection over a 10^3 surface concentration, from 0.03 to 30 pmol.cm^{-2}.
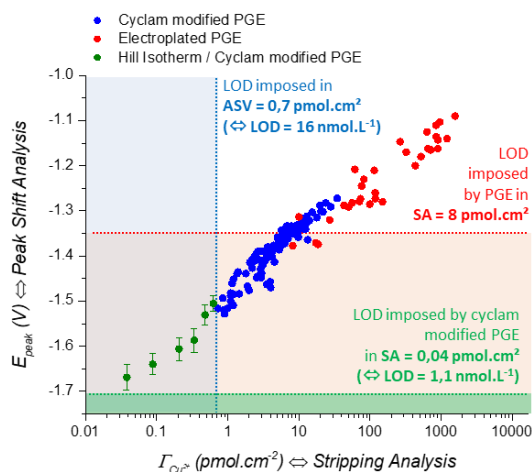
Fig. 6 Influence of the surface concentration of copper on the peak potential for proton reduction, depending on the electrode : red points report the results obtained with copper electroplated on unmodified PGE, blue points report the results obtained with copper accumulated at E_{oc} on cyclam modified electrode for whom Γ_{Cu} are calculated from the copper oxidation peak and green points are results obtained with copper accumulated at E_{oc} on cyclam modified electrode for which Γ_{Cu2+} were evaluated from Hill isotherms.

At last, our method was applied for more realistic situation for further use, i.e. in a pseudo-marine environment or in presence of other metal ions. We thus used artificial seawater (i.e a medium with the same ionic strength and pH, but without any trace of heavy metal and organic material) to demonstrate the feasibility of the measurement in real seawater sample. Indeed, total copper concentration determination in marine water is usually performed by acidifying the sample with HCl for storage (final pH < 2). Acidification has the advantage of limiting copper adsorption onto surfaces and to digest the organic matter which traps the cupric ions.

In this work, copper sensing experiments using SA performed after pre-concentration in artificial seawater at pH = 8.2 showed no difference compared to experiments performed in Milli-Q water (Fig. 5B), as expected [21-22]. Considering the volcano curve for HER on metal electrode and the potential metal ions that can bind to cyclam [57], it appears that Ni^{2+}, Co^{2+} and Zn^{2+} are natural copper competitors (log $K_{a,sol}$= 22.2, 12.7 and 15.5 respectively [22]) that can produce a catalytic signal during an analysis, similar to the copper one. The interference of these metals was therefore evaluated in artificial seawater. Accumulations were performed in 100 nmol.L^{-1} solutions of Ni^{2+}, Co^{2+} and Zn^{2+} and the electrodes were cycled in sodium sulfate at pH = 3 to evaluate HER with these different metals in solution. As shown in Fig. SI.9, CVs showed little variation of the peak potential for proton reduction compared to that obtained with Cu^{2+}. This observation may be fully ascribed to the better cyclam selectivity for Cu^{2+}, so preventing intermetallic species to be created during the cathodic polarization of the electrode [58].
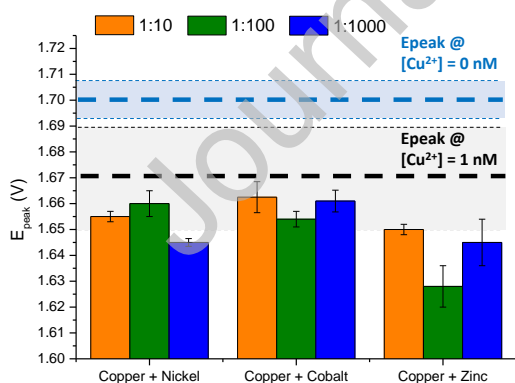

Fig. 7 Impact of high amount of competitor on the catalytic peak potential attributed to HER by chelated copper.

Experiments were also carried out to ensure the selectivity of the ligand for copper in natural conditions. For this, copper sensing with the SA method were performed in artificial seawater, spiked with 1 nmol.L^{-1} of copper and with various amounts of competitor (10, 10^2 and 10^3 higher concentration) although the large amount used here does not reflect the natural concentration of the competitors, which are naturally found in same order of magnitude than copper. As shown in Fig. 7, the competing metal ions induced little variation of the HER peak potential compared to the average of the single copper signal. This was expected given the higher affinity of the cyclam moiety towards Cu^{2+} than for the other cations. Furthermore, these results are very close to those obtained by Jasmin *et al.* [21] and Walcarius *et al.* [20], who demonstrated the very good selectivity of cyclam for copper sensing by AdASV.

4. Conclusions

This work mainly aimed at exploring how heterogeneous electrochemical catalysis may be an elegant manner to detect Cu^{2+} at the nanomolar level in solution. Since copper is known for catalysing proton reduction, HER was employed to precisely determine copper concentration thanks to electrocatalysis. The originality of this strategy has relied on the enhancement of the detection limit by indirectly measuring Cu^{2+} concentration from the shift of the electrocatalytic HER peak through the SA approach. So far, this strategy has never been used for such a purpose. Hence, after full optimization of the experimental conditions in terms of pH and supporting electrolyte, the three-part work (HER catalytic signal $\leftrightarrow$ Cu(II) surface concentration $\leftrightarrow$ Cu(II) solution concentration) was shown to be very effective since a LOD of 1.1 nmol.L^{-1} was achieved from SA analysis. This value is competitive to those found by

the classical VIP and ElViDor [59] approaches (0.95 nmol.L^{-1} and 2.0 nmol.L^{-1}, respectively). Another positive aspect of our strategy is that SA can be fully combined to AdASV within a single measurement and allows detection for higher concentration (> 10 nM), yielding a dual sensing method. A third advantage is that the chelating bifunctional cyclam ligand which was specifically chosen under its *C*-functionalized version, was shown to be highly selective towards Cu^{2+} compared to other divalent cations (Ni^{2+}, Co^{2+} and Zn^{2+}). At last, the simplicity of preparation, the robustness of the covalent grafting, the possible miniaturization of the system, the possibility of re-using the modified electrodes by an ASV step, the low risk of eutrophication and the low consumption of reactant (only proton) make this process very attractive for field measurements in both fresh water and marine environments.

Many perspectives can be now imagined from this proof-of-concept. Indeed, this new approach based on SA may also be extended to other metals by changing the chelating ligand to be immobilized. Other catalytic reactions than HER allowing the employment of SA can be envisaged. For instance, several Co^{2+} species have been reported as excellent electrocatalysts for O_2 reduction [60]. In the meantime, Ni-cyclam complexes are well-known for being able to perform catalytic CO_2 reduction in aqueous media at low overpotential [61]. One main challenge will be to find a metal catalyst which displays high turnover frequency combined with a high chelating strength after immobilization such that LOD will be as low as possible.

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Credit Author Statement

Lylian Challier : Conceptualization, Investigation, Supervision, Visualization, Writing - Original Draft, Writing - Review & Editing

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. Notes and references

[1] G. Peers, N.M. Price, Copper-containing plastocyanin used for electron transport by an oceanic diatom, Nature. 441 (2006)

[2] D. Horn, A. Barrientos, Mitochondrial copper metabolism and delivery to cytochrome C oxidase, IUBMB Life. 60 (2008) 421–429.

[3] J.B. Arellano, J.J. Lopez-Gorge, M. Baron The donor side of photosystem II as the copper-inhibitory binding site Photosynth. Res., 45 (1995), pp. 127-134

[4] P.P. Leal, C.L. Hurd, S.G. Sander, E. Armstrong, P.A. Fernández, T.J. Suhrhoff, M.Y. Roleda, Copper pollution exacerbates the effects of ocean acidification and warming on kelp microscopic early life stages, Sci. Rep. 8 (2018).

[5] P.P. Leal, C.L. Hurd, S.G. Sander, E. Armstrong, P.A. Fernández, T.J. Suhrhoff, M.Y. Roleda, Copper pollution exacerbates the effects of ocean acidification and warming on kelp microscopic early life stages, Sci. Rep. 8 (2018).

[6] USEPA 1986. Quality criteria for water. US Environmental Protection Agency, Washington D.C.

[7] Cairns et al., 1978 J. Cairns, A.L. Buikema, A.G. Heath, B.C. Parker Effects of Temperature on Aquatic Organism Sensitivity to Selected Chemicals Virginia Water Resources Research Center (1978)

[8] G. Dulaquais, M. Waeles, J. Breitenstein, J. Knoery, R. Riso, Links between size fractionation, chemical speciation of dissolved copper and chemical speciation of dissolved organic matter in the Loire estuary, Environ. Chem. 17 (2020) 385–399.

[9] M. Gledhill, M. Nimmo, J.H. Stephen, M.T. Brown The toxicity of copper (II) species to marine algae, with particular reference to macroalgae J. Phycol., 33 (1997), pp. 2-11

[10] M.M. Abualhaija, H. Whitby, C.M.G. van den Berg, Competition between copper and iron for humic ligands in estuarine waters, Mar. Chem. 172 (2015) 46–56.

[11] K. Gibbon-Walsh, P. Salaün, C.M.G. Van Den Berg, Pseudopolarography of copper complexes in seawater using a vibrating gold microwire electrode, J. Phys. Chem. A. 116 (2012) 6609–6620.

[12] P.L. Croot, J.W. Moffett, G.W.L. Iii, Polarographic determination of half-wave potentials for copper-organic complexes in seawater, Mar. Chem. 67 (1999) 219-232.

[13] M. Lou Tercier, J. Buffle, F. Graziottin, A Novel Voltammetric In-Situ Profiling System for Continuous Real-Time Monitoring of Trace Elements in Natural Waters, Electroanalysis 10 (1998) 355–363.

[14] C.B. Braungardt, E.P. Achterberg, B. Axelsson, J. Buffle, F. Graziottin, K.A. Howell, S. Illuminati, G. Scarponi, A.D. Tappin, M. Lou Tercier-Waeber, D. Turner, Analysis of dissolved metal fractions in coastal waters: An inter-comparison of five voltammetric in situ profiling (VIP) systems, Mar. Chem. 114 (2009) 47–55.

[15] Cathalot, C., Heller, M. I., Dulaquais, G., Waeles, M., Coail, J. -Y., Kerboul, A., et al. ELVIDOR- vibrating gold micro-wire electrode: In situ high resolution measurements of Copper in marine environments, Goldschmidt Abstracts (2017).

[16] M. Liu, D. Pan, W. Pan, Y. Zhu, X. Hu, H. Han, C. Wang, D. Shen, In-situ synthesis of reduced graphene oxide/gold nanoparticles modified electrode for speciation analysis of copper in seawater, Talanta 174 (2017) 500–506.

[17] Y. Zuo, J. Xu, F. Jiang, X. Duan, L. Lu, G. Ye, C. Li, Y. Yu, Utilization of AuNPs dotted S-doped carbon nanoflakes as electrochemical sensing platform for simultaneous determination of Cu (II) and Hg (II), J. Electroanal. Chem. 794 (2017) 71–77.

[18] G. March, T.D. Nguyen, B. Piro, Modified electrodes used for electrochemical detection of metal ions in environmental analysis, Biosensors. 5 (2015) 241–275.

[19] A. Garciá-Miranda Ferrari, P. Carrington, S.J. Rowley-Neale, C.E. Banks, Recent advances in portable heavy metal electrochemical sensing platforms, Environ. Sci. Water Res. Technol. 6 (2020) 2676–2690.

[20] S. Goubert-Renaudin, M. Etienne, Y. Rousselin, F. Denat, B. Lebeau, A. Walcarius, Cyclam-functionalized silica-modified electrodes for selective determination of Cu(II), Electroanalysis. 21 (2009) 280–289.

[21] J.P. Jasmin, K. Ouhenia-Ouadahi, F. Miserque, E. Dumas, C. Cannizzo, A. Chaussé, Straightforward grafting approach for cyclam-functionalized screen-printed electrodes for selective Cu(II) determination, Electrochim. Acta. 200 (2016) 115–122.

[22] S. Goubert-Renaudin, M. Etienne, S. Brandès, M. Meyer, F. Denat, B. Lebeau, A. Walcarius, Factors affecting copper(II) binding to multiarmed cyclam-grafted mesoporous silica in aqueous solution, Langmuir. 25 (2009) 9804–9813.

[23] B. Feier, I. Fizesan, C. Mériadec, S. Ababou Girard, C. Cristea, R. Sandulescu, F. Geneste, Influence of the electrografting method on the performances of a flow electrochemical sensor using modified electrodes for trace analysis of copper (II), J. Electroanal. Chem. 744 (2015) 1–7.

[24] W. Ben Mefteh, Y. Chevalier, C. Bala, N. Jaffrezic-Renault, Voltammetric Detection of Copper Ions on a Gold Electrode Modified with a N-methyl-2-naphthyl-cyclam film, Anal. Lett. 51 (2018) 971–982.

[25] W. Ben Mefteh, H. Touzi, Y. Chevalier, F. Bessueille, R. Kalfat, N.J. Renault, Gold electrodes functionalized by methyl-naphthyl substituted cyclam films for the detection of metal ions, Sensors Actuators, B Chem. 213 (2015) 334–342.

[26] S. Mahouche Chergui, N. Abbas, T. Matrab, M. Turmine, E. Bon Nguyen, R. Losno, J. Pinson, M.M. Chehimi, Uptake of copper ions by carbon fiber/polymer hybrids prepared by tandem diazonium salt chemistry and in situ atom transfer radical polymerization, Carbon 48 (2010) 2106–2111.

[27] A. Kaliyaraj Selva Kumar, Y. Zhang, D. Li, R.G. Compton, A mini-review: How reliable is the drop casting technique, Electrochem. Commun. 121 (2020).

[28] Y. Dong, L.F. Lindoy, P. Turner, G. Wei, Three-ring, branched cyclam derivatives and their interaction with nickel(II), copper(II), zinc(II) and cadmium(II), Dalton Trans. (2004) 1264–1270.

[29] N. Camus, N. Le Bris, S. Nuryyeva, M. Chessé, D. Esteban-Gómez, C. Platas-Iglesias, R. Tripier, M. Elhabiri, Tuning the copper(II) coordination properties of cyclam by subtle chemical modifications, Dalton Trans. 46 (2017) 11479–11490.

[30] S. Liu, Y.J. Lei, Z.J. Xin, Y. Bin Lu, H.Y. Wang, Water splitting based on homogeneous copper molecular catalysts, J. Photochem. Photobiol. A Chem. 355 (2018) 141–151.

[31] M. Kügler, J. Scholz, A. Kronz, I. Siewert, Copper complexes as catalyst precursors in the electrochemical hydrogen evolution reaction, Dalton Trans. 45 (2016) 6974–6982.

[32] J. Du, J. Wang, L. Ji, X. Xu, Z. Chen, A Highly Active and Robust Copper-Based Electrocatalyst toward Hydrogen Evolution Reaction with Low Overpotential in Neutral Solution, ACS Appl. Mater. Interfaces. 8 (2016) 30205–30211.

[33] S. Majumder, A. Abdel Haleem, P. Nagaraju, Y. Naruta, A new preparation of a bifunctional crystalline heterogeneous copper electrocatalyst by electrodeposition

using a Robson-type macrocyclic dinuclear copper complex for efficient hydrogen and oxygen evolution from water, Dalton Trans. 46 (2017) 9131–9139.

[34] X. Liu, S. Cui, Z. Sun, P. Du, Robust and highly active copper-based electrocatalyst for hydrogen production at low overpotential in neutral water, Chem. Commun. 51 (2015) 12954–12957.

[35] X. Liu, H. Zheng, Z. Sun, A. Han, P. Du, Earth-abundant copper-based bifunctional electrocatalyst for both catalytic hydrogen production and water oxidation, ACS Catal. 5 (2015) 1530–1538.

[36] S.R. Hosseini, S. Ghasemi, S.A. Ghasemi, Effect of surfactants on electrocatalytic performance of copper nanoparticles for hydrogen evolution reaction, J. Mol. Liq. 222 (2016) 1068–1075.

[37] T.T. Li, S. Cao, C. Yang, Y. Chen, X.J. Lv, W.F. Fu, Electrochemical water oxidation by in situ -generated copper oxide film from [Cu(TEOA)(H2O)2][SO4] complex, Inorg. Chem. 54 (2015) 3061–3067.

[38] C. Lu, J. Wang, Z. Chen, Water Oxidation by Copper–Amino Acid Catalysts at Low Overpotentials, ChemCatChem. 8 (2016) 2165–2170.

[39] J. Wang, L. Zhu, L. Ji, Z. Chen, Preparation of nanostructured Cu(OH)2 and CuO electrocatalysts for water oxidation by electrophoresis deposition, J. Mater. Res. 33 (2018) 581–589.

[40] C. Lu, J. Du, X.J. Su, M.T. Zhang, X. Xu, T.J. Meyer, Z. Chen, Cu(II) Aliphatic Diamine Complexes for Both Heterogeneous and Homogeneous Water Oxidation Catalysis in Basic and Neutral Solutions, ACS Catal. 6 (2016) 77–83.

[41] X. Liu, H. Jia, Z. Sun, H. Chen, P. Xu, P. Du, Nanostructured copper oxide electrodeposited from copper(II) complexes as an active catalyst for electrocatalytic oxygen evolution reaction, Electrochem. Commun. 46 (2014) 1–4.

[42] X. Liu, S. Cui, M. Qian, Z. Sun, P. Du, In situ generated highly active copper oxide catalysts for the oxygen evolution reaction at low overpotential in alkaline solutions, Chem. Commun. 52 (2016)

[43] A. Walcarius, Electrocatalysis, sensors and biosensors in analytical chemistry based on ordered mesoporous and macroporous carbon-modified electrodes, TrAC - Trends Anal. Chem. 38 (2012) 79–97.

[44] Y. Wu, S. Ali, R.J. White, Electrocatalytic Mechanism for Improving Sensitivity and Specificity of Electrochemical Nucleic Acid-Based Sensors with Covalent Redox Tags - Part i, ACS Sensors. 5 (2020) 3833–3841

[45] J.M. Savéant Elements of Molecular and Biomolecular Electrochemistry : an Electrochemical Approach to Electron Transfer Chemistry Wiley-Interscience, New Jersey (2006)

[46] T. Breton, D. Bélanger, Modification of carbon electrode with aryl groups having an aliphatic amine by electrochemical reduction of in situ generated diazonium cations, Langmuir. 24 (2008) 8711–8718.

[47] P.K. Tarafder, D.P.S. Rathore, Spectrophotometric determination of nitrite in water, Analyst. 113 (1988) 1073–1076.

[48] Aminot, A. ; Kérouel, R. 2004. Hydrologie des écosystèmes marins. Paramètres et analyses. In Ifremer (ed), France.

[49] M. Ujvari, G. Lang, On the stability of perchlorate ions against reductive attacks in electrochemical systems and in the environment, J. Electrochem. Sci. Eng. (2011).

[50] S. Nestke, M. Kügler, J. Scholz, M. Wilken, C. Jooss, I. Siewert, A Copper Complex as Catalyst in Proton Reduction, Eur. J. Inorg. Chem. 2017 (2017) 3376–3382.

[51] A.C. Arulrajan, C. Renault, S.C.S. Lai, How changes in interfacial pH lead to new voltammetric features: The case of the electrochemical oxidation of hydrazine, Phys. Chem. Chem. Phys. 20 (2018) 11787–11793.

[52] S. Horvath, L.E. Fernandez, A.M. Appel, S. Hammes-Schiffer, PH-dependent reduction potentials and proton-coupled electron transfer mechanisms in hydrogen-producing nickel molecular electrocatalysts, Inorg. Chem. 52 (2013) 3643–3652.

[53] M. Zeng, Y. Li, Recent advances in heterogeneous electrocatalysts for the hydrogen evolution reaction, J. Mater. Chem. A. 3 (2015) 14942–14962.

[54] L. Koopal, W. van Riemsdijk, J. de Wit, M. Benedetti, Analytical isotherm equations for multicomponent adsorption to heterogeneous surfaces, J. Colloid Interface Sci., 166 (1) (1994), pp. 51-60

[55] B. Piro, S. Reisberg, V. Noel, M.C. Pham, Investigations of the steric effect on electrochemical transduction in a quinone-based DNA sensor, Biosens. Bioelectron. 22 (2007) 3126–3131.

[56] M.A. Al-Ghouti, D.A. Da'ana, Guidelines for the use and interpretation of adsorption isotherm models: A review, J. Hazard. Mater. 393 (2020).

[57] Y. Yan, B.Y. Xia, B. Zhao, X. Wang, A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting, J. Mater. Chem. A. 4 (2016) 17587–17603.

[58] O.W. Lau, O.M. Cheng, Determination of zinc in environmental samples by anodic stripping voltammetry, Anal. Chim. Acta. 376 (1998) 197–207.

[59] M.M. Grand, A. Laes-Huon, S. Fietz, J.A. Resing, H. Obata, G.W. Luther, A. Tagliabue, E.P. Achterberg, R. Middag, A. Tovar-Sánchez, A.R. Bowie, Developing autonomous observing systems for micronutrient trace metals, Front. Mar. Sci. 6 (2019).

[60] [1] H. Arima, M. Wada, T. Nakazono, T. Wada, Tuning Oxygen Reduction Catalysis of Dinuclear Cobalt Polypyridyl Complexes by the Bridging Structure, Inorg. Chem. 60 (2021) 9402–9415.

[61] J.D. Froehlich, C.P. Kubiak, Homogeneous CO_2 reduction by Ni(cyclam) at a glassy carbon electrode, Inorg. Chem. 51 (2012) 3932–3934.