Gold and silver anchored cobalt porphyrins used for catalytic water splitting

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HIGHLIGHTS

- A Co porphyrin attached to a gold electrode is a robust system to obtain H_2 from H_2O.
- The redox potential for both oxidation and reduction of water is decreased by 200 mV.
- In aqueous buffers, the current increases with decreasing pH.
- Efficient electrocatalyst for water split, focused H_2 production.

GRAPHICAL ABSTRACT
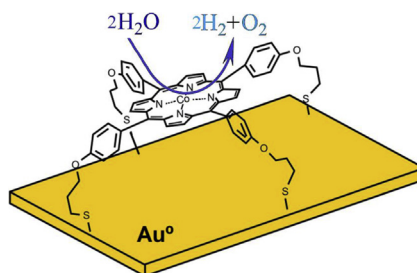
ARTICLE INFO

ABSTRACT

In natural photosynthesis, the energy in sunlight is used to rearrange the bonds present in water to produce oxygen and hydrogen. Artificial systems that perform water splitting require catalysts that assist the production of hydrogen from water without excessive reduction potential.

Consequently a cobalt porphyrin({cobalt[II]-5,10,15,20-tetrakis[3-(p-acetylthiopropoxy) phenyl] porphyrin}[Co—P]) covalently bound to gold or silver has been tested as a catalyst for reduction and oxidation of H_2O to H_2 and O_2, respectively. In the cyclic voltammogram Co^{III}/Co^{II} and Co^{II}/Co^{I} reversible waves were observed at potentials close to the expected values. The addition of water increased the cathodic peak for the Co^{II}/Co^{I} wave, consistent with the electrocatalytic reduction of water. In aqueous buffers the current increased for catalytic [Co—P] with decreasing pH. Similar results are obtained by changing the solvent or metal electrode to which the porphyrin is adsorbed. This leads to a reduction in the redox potential for the H^+/H_2 couple by 200 mV.

The material ($Au°$—[Co—P]) shows good efficiency and robustness for the electrochemical production of H_2 in different solvents and buffers in contrast to results previously seen for other porphyrins in solutions. The modified electrode $Au°$—[Co—P] shows high stability, and it is not damaged after several cycles. It can be stored in a CH_2Cl_2 solution and reused several times.

1. Introduction

Energy storage, by electrochemical or photochemical reduction of water to hydrogen, requires catalysis for the evolution of H_2 because of the high activation energy necessary for the O—H bond cleavage. Platinum is an excellent catalyst for this purpose and is very widely used in studies of water splitting. Disadvantages of platinum include its cost and the ease of which it can be poisoned by contaminants, such as sulfur compounds, present in the solvent. Therefore it would be interesting to develop molecular catalysts for H_2 evolution in order to achieve cleaner and less expensive water splitting. More specifically, compounds covalently adsorbed on

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surfaces as monolayers can be effective catalysts for this purpose, and minuscule amounts are needed to cover large surface areas.

Spiro et al. [1] has shown catalytic formation of H_2 by the use of Co^I porphyrins in solution. Metalloporphyrins have also been extensively studied for other uses in technical applications [2–16] such as gas sensors [17,18] and catalysis [19–21] coupled to surfaces. Monolayers of porphyrins and metalloporphyrins on inert metal surfaces have been used as suitable models for the study of the electronic structure and reactivity of different systems [22–28]. These types of thin film systems have been used to study direct metalation [24,27,28], coordination, and ligand reactions [26]. Metalloporphyrins are also very useful as agents for the modification of electrodes due to their easy deposition [29,30] and their behavior in different chemical environments. Interestingly, direct electron transfer from a silver surface to a Co-adsorbed porphyrin has been recently shown by X-ray photoelectron spectroscopy (XPS). This interaction could be modulated by NO coordination [31–45] and has also been predicted for a gold electrode [16] by DFT calculations.

One of the most successful methods for binding molecules to surfaces is based on the creation of gold–sulfur bonds. A large number of monomers like porphyrins or thiols are prepared and bound to gold electrodes by this method [31–36]. To avoid problems associated with the formation of disulfide bonds, the sulfur is in a protected form (for example with an S-acetyl protecting group) [38,39], which undergoes *in situ* cleavage on the surface [33]. This technique is simpler than the evaporative deposition and does not require the use of a quartz microbalance to obtain a single layer.

On the other hand, cobalt complexes are attractive candidates for such catalysts in the form of Co^I, since it is a potent nucleophile that can be protonated easily. In this work we have used cobalt[II]-5,10,15,20-tetrakis[3-(p-acetylthiopropoxy)phenyl]porphyrin ([Co–P], Fig. 1A). This porphyrin can be immobilized on gold and silver by formation of strong metal-sulfur bonds, adapting a conformation parallel to the surface (Fig. 1B) [16].

In this study we examined the electrocatalytic behavior of [Co–P] in order to develop an efficient electrocatalyst for water splitting and focused H_2 evolution.

2. Materials and methods

2.1. Chemicals

[Co–P] was purchased from Frontier Scientific and used as received. Ferrocene (Fc), $N(Bu)_4PF_6$ and KNO_3 were purchased from Sigma–Aldrich. Acetonitrile (AcCN), DMSO, and other organic solvents used were spectroscopic grade. These solvent were distilled from appropriate drying agents (CaH_2) under argon just prior to use. Water, Milli-Q grade, and argon of high purity were used.

2.2. Instruments

Cyclic voltammetry and amperometric measurements were carried out with a TEQ 03 potentiostat. For voltammetry in non-aqueous or organic solvent media (CH_2Cl_2, DMSO or AcCN) a three-electrode system was used, consisting of two platinum electrodes, and either a working gold or silver electrode; the supporting electrolyte (SE) was $N(Bu)_4PF_6$ (0.1 M). De-aeration of all solutions was accomplished by passing a stream of high-purity argon through the solution for 10 min and maintaining a blanket of inert gas over the solution while making the measurements. The inert gas was saturated with the appropriate solvent before entering the cell to minimize the evaporation of solvent from the cell. The potential was measured against ferrocene (Fc) as pseudo-reference and converted to SCE potentials by using E(SCE) = E(Ferrocene) - + 320 mV.

Cyclic voltammetry for the cobalt–porphyrin modified electrodes or for the bare gold electrodes used as controls was performed by using the corresponding electrode as the working electrode. In aqueous solution, a KCl saturated $Ag°/AgCl$ electrode was used as the reference electrode and a platinum wire as the counter electrode (supporting electrolytes were KNO_3 and $KClO_4$ 0.1 M, pH 6). Solutions in the cell were changed periodically to avoid contamination from entering the cell via Ag/AgCl, as Cl^- anions may interfere with measurements.

The midpoint potentials ($E_{1/2}$) values were measured as that potential lying midway between the oxidation and reduction peak for a given couple. All experiments were carried out at room temperature. In water solution the potential was measured against a Ag/AgCl reference and converted to SCE potentials by using E(SCE) = E(Ag/AgCl) + 45 mV.

2.3. Electrode preparation

Before each experiment, the surface of the gold and silver electrodes was first polished with alumina powder (diameter 0.3
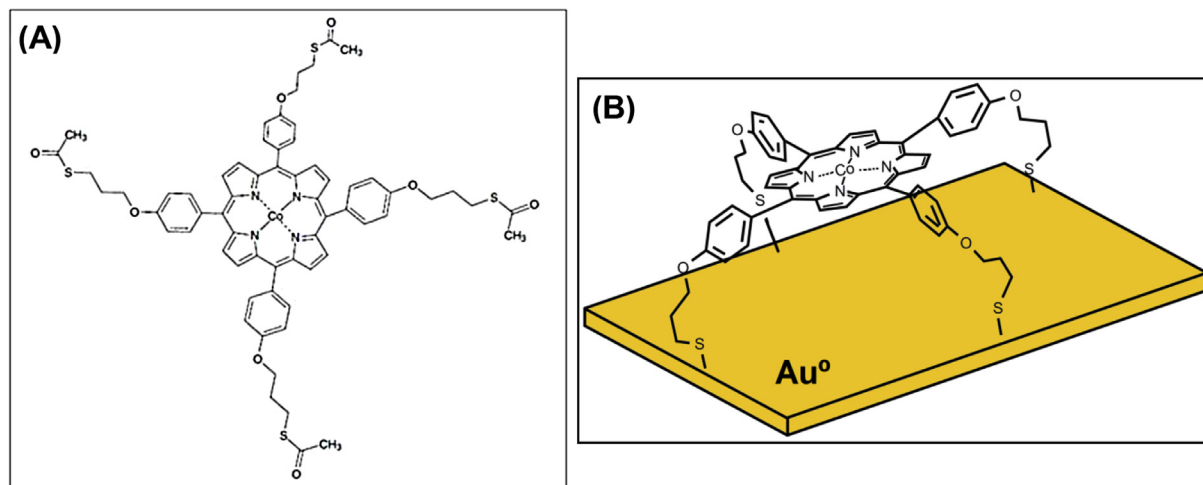

Fig. 1. (A) Cobalt[II]-5,10,15,20-tetrakis[3-(p-acetylthiopropoxy)phenyl]porphyrin[Co–P]. (B) [Co–P] anchored on a surface.

and 0.05 μm) and rinsed with pure water. Then the electrodes were cleaned in "Piranha" solution [H₂SO₄:H₂O₂ (30% aq.), 2:1] for 5 min. After copious rinsing with Milli-Q water the Au electrodes were electrochemically cleaned by potential cycling in 0.5 M H₂SO₄ in the range of 0 and 1500 mV vs. Ag°/AgCl until a typical cyclic voltammogram of clean gold was obtained. After rinsing with distilled water and ethanol and drying, the electrodes was ready to be modified.

The modification was carried out by immersing the gold and silver electrode in a solution of [Co−P] 0.5 mM in dichloromethane for 24 h, after which [Co−P] was anchored to the gold electrode and was ready for the measurements. The porphyrin covers 25−30% of the surface, as determined in our previous work [16]. The Co−P solution was reused several times. Water (Milli-Q quality) was added to dry AcCN solutions to perform the cyclic voltammetries in the presence of water.

2.4. H₂ production measurements

The potentiostat was used as described above. Amperometric measurements around the overpotential value were performed. The solvent used was a formate buffer (pH = 3). Amperometric experiments for the cobalt−porphyrin modified electrodes or for the bare gold electrodes used as controls were performed by using the corresponding electrode as the working electrode. In aqueous solution, Ag°/AgCl electrode was used as the reference electrode and a platinum wire as the counter electrode.

H₂ production was measured by connecting the electrochemical cell with a gas burette. The current vs. time measurements were performed at different overpotentials: −500 mV, −600 mV and −700 mV vs. Ag°/AgCl, in order to assess the durability and robustness of [Co−P]. For overpotential values more negative than −700 mV current saturation was observed.

3. Results and discussion

The physicochemical study of the [Co^{II}−P] electrode was previously done by our group [16]. The Co couples were described as follows [16]; five redox couples are found for Co(P), corresponding to the following reactions (Fig. 2):
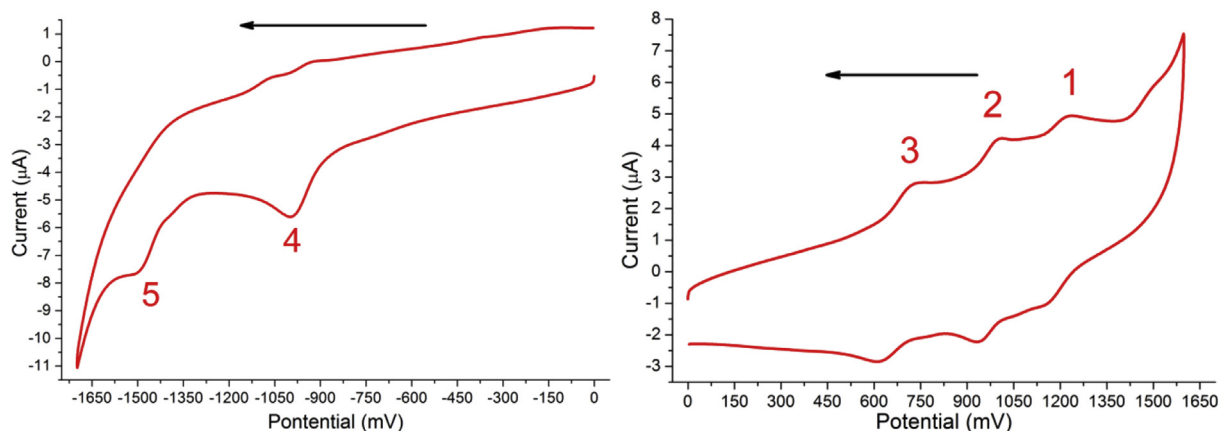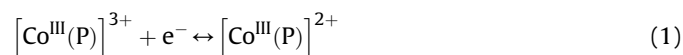
$$\left[Co^{III}(P)\right]^{3+} + e^- \leftrightarrow \left[Co^{III}(P)\right]^{2+} \tag{1}$$

$$\left[Co^{III}(P)\right]^{2+} + e^- \leftrightarrow \left[Co^{III}(P)\right]^{+} \tag{2}$$

Table 1
Values of redox potentials obtained from cyclic voltamograms for gold and silver electrodes modified with [Co−P] in DMSO and AcCN, vs. SCE.

Solvent	Couple	Gold	Silver
		$E_{1/2}$ o E_{irr} (ΔI)	E_{irr}
DMSO	**Co^{II}/Co^{I}**	−720 mV (5.2 μA)	−
AcCN[a]	**Co^{II}/Co^{I}**	−1206 mV (121.3 μA)	−578 mV (0.58 mA)

[a] Both cyclic voltammetries (silver) were made from 500 to −850 mV. The reference was run in the presence of ferrocene (Fc) and iodine with 0.1 M Bu₄NPF₆. The difference in reduction potential for Fc vs. SCE is 320 mV.

$$\left[Co^{III}(P)\right]^{+} + e^- \leftrightarrow Co^{II}(P) \tag{3}$$

$$Co^{II}(P) + e^- \leftrightarrow \left[Co^{I}(P)\right]^{-} \tag{4}$$

$$\left[Co^{I}(P)\right]^{-} + e^- \leftrightarrow \left[Co^{I}(P)\right]^{2-} \tag{5}$$

The first three reactions correspond to one electron oxidations starting from the Co^{II}(P) redox state (1, 2 and 3); and the other two (4 and 5) correspond to two one-electron reductions [16]. Waves 1 and 2 represent oxidations on the porphyrin ring. The waves to which we refer from now on will be the Co^{III}/Co^{II} and Co^{II}/Co^{I} redox couples (eqs. (3) and (4)).

Cyclic voltammetry and amperometry were carried out in different solvents in the presence and absence of water, as well as in various buffers. Table 1 shows the cobalt redox couples for gold and silver modified electrodes. It is observed that in dry acetonitrile the separation in reduction potentials of the **Co^{II}/Co^{I}** and **Co^{III}/Co^{II}** redox couples get smaller for the silver electrode: the difference between the couples in acetonitrile is reduced from 1300 mV for gold to 300 mV for silver. This could be due to axial coordination of the solvent [46−48] or the electron-donating ability of the electrode to the porphyrin and one might think that the metal surface is "coordinated" to the **Co** metal center (in the sense that receives or donates electron density as suggested by Gottfried et al.) [24]. This effect is more important for the silver electrode, but unfortunately in this case the attachment was not robust enough and could stand only one cycle (Fig. S.4) after which the porphyrin was apparently unanchored from the electrode.

As it is well known the Ag−S bond is very strong, since silver is "sulfiphilic". However, the negative reduction potential of −850 mV reduces the S−Ag bond, "un-anchoring" the porphyrin (Fig. S.4).

Fig. 2. Cyclic voltammograms in a CH₂Cl₂ solution of [Co−P] (scanrate = 100 mV/s). Pseudo reference electrode: platinum (reference: ferrocene); working electrode: Au° polycrystalline; counter electrode: platinum; supporting electrolyte: PF₆N(Bu)₄ 0.1 M. The redox potential (mV) is reported against SCE [16].

Therefore, the silver electrode is not robust enough as to be used in several cycles. This does not happen with gold, which has a much lower reduction potential. The gold electrode showed to be quite robust, being unaltered ever after 20 cycles. The stability was not only tested by running multiple cycles, the electrode can be reused several times.

The modified gold electrode with **[Co^{II}–P]** was tested first in dry acetonitrile and by addition of 2% of water. It can be observed that when water is added in the presence of porphyrin the catalytic wave at 1240 mV assigned to water oxidation rises markedly due to the porphyrin-catalyzed oxidation of water. Also, noteworthy is that the wave observed at approximately −1200 mV, belonging to the **Co^{II}/Co^{I}** couple, is shifted to −655 mV and intensified by the presence of water (see Fig. 3, green circles). These results are in agreement with the work by Spiro and coworkers [1], carried out with a similar metalloporphyrin (TPP), but in solution.

The abovementioned results are a good indication of the capacity of [Co–P] to both oxidize and reduce water. Taking into account the capacity of [Co–P] to improve the catalytic activity, we decided to perform other tests that will be described below.

The modified gold electrode with **[Co^{II}–P]** was tested first in dry DMSO and then the measurements were repeated with each experiment with increasing amounts of water, from 0.5% to 2% (see S.1 for other water percentages). Table 2 and Fig. 4 shows the comparison between DMSO and acetonitrile when 2% water is added. Excellent activity was observed for the [Co–P] catalyst. In both solvents there is an increase in the intensity of the wave corresponding to **Co^{II}/Co^{I}**, while the **Co^{III}/Co^{II}** couple is not altered. A similar pattern was observed when the experiments were carried out with the dissolved porphyrin (1 × 10^{-4} M); the waves occur at the same redox potential and the wave corresponding to the **Co^{II}/Co^{I}** redox couple is increased by addition of water. Also, it can be observed that the oxidation of water is shifted from 1240 mV in acetonitrile to ca. 718 mV in the case of DMSO, demonstrating again the capacity of [Co–P] to not only catalyze water reduction, but also water oxidation.

3.1. Measurements at different pH values

Measurements were taken using the modified silver and gold electrodes (Fig. S.6) by using three different solutions (Table 3): borate (pH = 10), potassium nitrate (pH = 7) and formate (pH = 3).
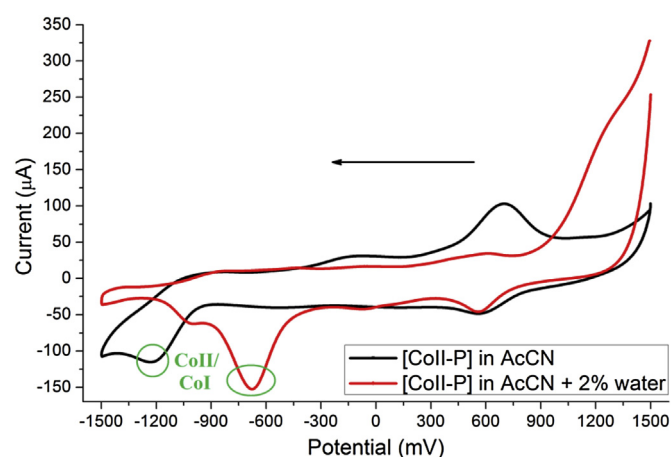
The blank was made with the gold electrode prior to the deposition of the porphyrin. The results obtained at pH = 3 are displayed in Fig. 5.

Measurements at pH = 3 were obtained by use of aqueous formate buffer solution both in the presence and absence (blank) of [Co–P]. The catalytic wave moves to less negative potential values in the presence of [Co–P], from (−700 mV) blank to (−580 mV), demonstrating the activity of our catalyst in aqueous media. The results in buffer solutions match those observed before [1], but with the covalently attached modified electrodes it was possible to measure a larger potential window (almost double).

Comparing the values obtained by the Nernst equation shown below [46]:

$$E = E_{1/2} - \frac{0.0592}{n^\circ e^-} log \frac{[H_2D]}{[A]} - 0.0592 \times pH \qquad (1)$$

Being "E" the Nernst reduction potential Co^{II}/Co^{I}, E$_{1/2}$ the standard reduction potential, [H$_2$D] is the electron donor, and [A] the electron acceptor. Using the value reported by Suaréz et al [16], E$_{1/2}$ = −850 mV vs. SCE for the same metalloporphyrin, E(Co^{II}/Co^{I}) = −1442 mV at pH = 10, −1264 mV at pH = 7 and −1028 mV at pH = 3. These values are far more negative than the ones observed in Table 3. On the other hand the change in E(Co^{II}/Co^{I}) ~ +400 mV from pH 10 to 3 described by the Nernst equation, is not observed experimentally for Au$^\circ$–[Co–P] and Ag$^\circ$–[Co–P], probably due to ionic effects attributed to the different buffers.

In the case of the gold electrode a 270 mV shift is observed for the catalytic wave with decreasing pH. For the modified silver electrode this effect is reversed (but smaller). The proposed mechanism for the catalytic reduction of water (see Fig. 6) [1] involves formation of a cobalt hydride (that can be postulated as Co(II)–H or Co(III)–H$^-$), by reaction of a proton with the reduced Co(I)porphyrin. The cobalt hydride Co(III)–H$^-$ can be attacked by a proton to produce [Co(III)P] and H$_2$. This is probably the major pathway, since the reaction of Co(II)–H with another Co(II)–H is unlikely, taking into account that the porphyrin molecules are fixed on the surface. Both [Co(III)P] and [Co(II)P] will be reduced back to [Co(I)P] under the experimental conditions.

3.2. Electrochemical kinetics for the gold electrode (Tafel calculations)

The measurement of an anodic and cathodic overpotential indicates an intrinsic activation barrier due to the electrode-solution interface (activation overpotential), and the limitations in the mass transport of reactant or product to or from the electrode. The activation overpotential is related to the potential difference above the equilibrium value required to produce a current which, in turn, depends on the activation energy of the redox event. The activation overpotentials are intrinsic properties of the catalysts used in the anode and cathode [47,48]. This overpotential is related logarithmically to the current density (j). The logarithmic ratio of the current density (log j) and the overpotential were used to evaluate the

Fig. 3. Cyclic voltammetry in the presence and absence of water (red and black curves respectively). Pseudo reference electrode: platinum (reference: ferrocene); working electrode: Au$^\circ$–[Co–P] (modified electrode); counter electrode: platinum; supporting electrolyte: PF$_6$N(Bu)$_4$ 0.1 M; scanrate 100 mV/s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Measurements for [Co–P] porphyrin deposited on gold in DMSO and CH$_3$CN with 2% water.

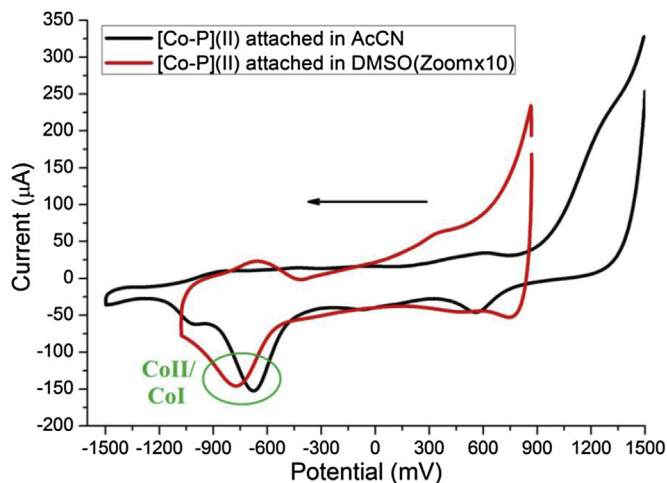| Solvent	Redox couple	E$_{1/2}$ (ΔI)	Catalytic wave (oxidation of water)
DMSO 2% water	**Co^{II}/Co^{I}**	−802 mV (148.2 μA)	≈718 mV
CH$_3$CN 2% water	**Co^{II}/Co^{I}**	−655 mV (162.2 μA)	≈1249 mV

Fig. 4. Cyclic voltammograms in AcCN and DMSO with 2% of water. Pseudo-reference electrode: platinum (reference: ferrocene); working electrode: Au°–[Co–P] (modified electrode); counter electrode: platinum; supporting electrolyte: $PF_6N(Bu)_4$ 0.1 M; scanrate 100 mV/s.

performance of the catalyst by plotting the steady state current densities under a variety of overpotential values (Tafel curves). However, any current density can be obtained for a catalyst by using large enough electrodes. For this reason, it is a common practice to normalize the current densities by dividing the current by the geometric surface area. Even with this standardization, the performance of an electrode will depend largely on the tridimensional nature of the substrate and catalyst used (surface roughness, for example). Substrate preparation of high surface area catalysts is a common method to improve performance. While this issue complicates accurate comparisons of the catalytic efficiency, the current density normalized to the geometric surface provides relevant data regarding the performance of the electrodes [48]. For an electrode reaction, the equilibrium is characterized by the Nernst equation, which relates the electrode potential with the concentration of the participants. In the case of electrode current, it is often limited in whole or in part by the rate at which electrons are exchanged at the electrode surface. In such systems (heterogeneous systems), the current (i) is often related exponentially to the overpotential, η, hence our use of the Tafel equation (eq. (2)):

$$\eta = a + b \log i \tag{2}$$

In order to obtain anode and cathode currents which produce a reduction and oxidation of [Co–P] and whereas reaction (1) is reversible, as shown in eq. (3), reduction potentials were applied for the oxidation and reduction windows (1640 mV–1820 mV and −860 mV to −620 mV respectively)

$$\left[Co(III) - P\right] \underset{V_b}{\overset{V_f}{\rightleftharpoons}} \left[Co(II) - P\right] \tag{3}$$
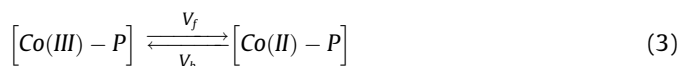
The rate, V_f, (forward velocity) should be proportional to the concentration at the electrode surface which is coated with [Co–P]. The concentration (C_o) is dependent on the distance, x, from the surface and the time, t, and is expressed as $C_O(x,t)$, hence the surface concentration is $C_O(0,t)$, (eq. (4)):

$$V_f = k_f C_O(0,t) = \frac{i_c}{nFA} \tag{4}$$

Since the forward reaction is a reduction there is a cathodic current, ic, proportional to V_f(final rate) and V_b (initial rate). Similarly, we have for the reverse reaction (eq. (5)):

$$V_b = k_b C_R(0,t) = \frac{i_a}{nFA} \tag{5}$$

where i_a is the anodic component, C_R (final concentration). The net reaction rate is given by eq. (6). (eq. (6) and Fig. S.7):

$$V_{net} = V_f - V_b = k_f C_O(0,t) - k_b C_R(0,t) = \frac{i}{nFA} \tag{6}$$

Using eq. (6) and the data obtained from amperometry experiments we can calculate the rate of the reaction, cathodic and anodic. For the oxidation reaction the obtained rate is $(9.28 \pm 0.56) \times 10^{11}$ mol s^{-1} cm^{-2}; for the reduction the rate is $(2.99 \pm 0.72) \times 10^{10}$ mol s^{-1} cm^{-2}; and the net velocity value is $(8.98 \pm 0.64) \times 10^{11}$ mol s^{-1} cm^{-2}.

Comparing the activity with other catalysts shown in Fig. 6 (using Tafel plots, see Figs. S.7 and S.8) our porphyrin has an interesting catalytic activity, because even the overpotential values are relatively large, high currents are observed. We have calculated the value of j_0 (normalized current density) according to the method describe by Nocera et al. [48]. For the [Co–P] modified gold electrode the value obtained for oxidation is: **$j_0 = 1.26$ A/cm^2** and for reduction: **$j_0 = -1.82$ A/cm^2**. For **$\eta = 0$** the parameters "a" and "b" for oxidation and reduction can be obtained: $a_{oxd} = 3.21$ A/cm^2; $a_{red} = -0.952$ A/cm^2 and $b_{oxd} = -0.13$ A/cm^{2}V; $b_{red} = 0.092$ A/cm^{2}V (see eq. (1)).

The [Co–P] porphyrin attached on a gold surface gives a value of **$log(j) = -1.6$** and **$\eta = 700$ mV**, and it is stable in organic solvents in the presence of water and in aqueous media, such as buffers at different pH. The value $log(j)$ is obtained by using the Tafel equation, in which the current ($\log i$) is replaced by the current density ($\log (j)$) (eq. (7)):

$$\eta = a + b \log (j) \tag{7}$$

The performance of the catalysts in non-aqueous solvents makes it difficult for benchmarking with other molecular catalysts

Table 3
Values of redox potentials obtained from cyclic voltammetry with gold and silver electrodes modified with [Co–P] in buffers (vs. SCE).[a]

Solvent (buffer)[a]	Wave	Gold		Silver	
		$E_{1/2}$ o E_{irr} Co^{II}/Co^{I}	Catalytic wave[b]	E_{irr} Co(II)/Co(I)	Catalytic wave
Borate pH = 10	Position (ΔI)	−650 mV (−0.45 mA)	−850 mV	−777 mV (−1.03 mA)	≈−784 mV
Nitrate pH = 7	Position (ΔI)	−790 mV (−0.35 mA)	−800 mV	−500 mV (−1.15 mA)	≈−808 mV
Formate pH = 3	Position (ΔI)	−700 mV (−0.75 mA)	−580 mV	−800 mV (−57.80 μA)	≈−823 mV

[a] The concentration of all buffers was about 0.1 M.
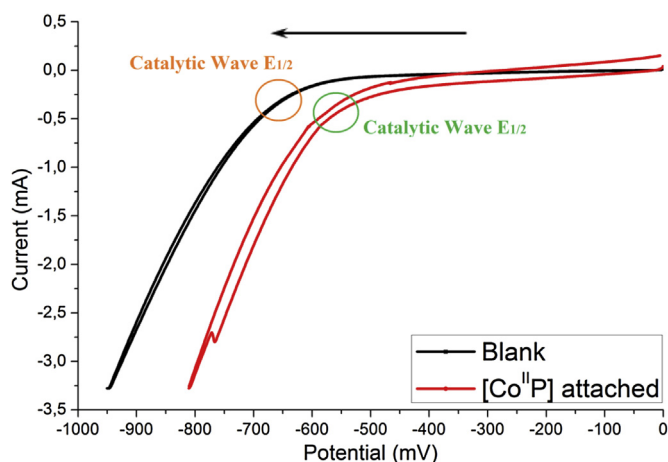[b] The reference electrode used was calomel.

Fig. 5. Cyclic voltammetry at pH = 3 for modified and bare gold electrodes. Reference electrode: Ag°/AgCl; working electrode: Au°–[Co–P] (modified electrode); counter electrode: Pt; supporting electrolyte: 0.1 M formate buffer in KNO₃; scan rate 100 mV/s.

due to the difficulty in measuring the activity of protons. However, recent reports detail a suitable treatment of the thermodynamics of the reduction of protons in non-aqueous solvents [48]. In our case, we can compare the value of the activity of our catalyst with previous studies described in reference [48]. Compound **24** in Fig. 7, a mixed Co^{II}/Pt^{II} porphyrin catalyst deposited on glassy carbon, could be compared to [Co–P]. Compound **24** catalyzes the reduction of protons at an overpotential of 600 mV and current densities of ~50 mA/cm² [47] at extremely low pH (pH = 0), as is to mentioned above while [Co^{II}–P] on gold reduces the hydrogen overpotential to **700 mV** with a current density of **−1.6** in acetonitrile with 2%

water. The overpotential is reduced even further to 600 mV at pH = 3 in formate buffer.

3.3. Efficiency of [Co–P] to form hydrogen (H₂)

Shown in Fig. 8 (A and B) are the current vs. time plots. The obtained volume of H₂ gas in the experiments shown in Fig. 8(B) is 2.03 ± 0.10 mL (average of 3 independent experiments). The same electrode was used in all experiments, demonstrating its durability and robustness, being active even after a total of ca. 200 min of electrolysis. A blank experiment was performed with the same parameters but with a bare gold electrode. All experiments were performed in triplicate. A pH change occurs in the solution, changing from 2.92 to 3.49. This indicates that protons are consumed to produce H₂. With the data obtained, we can calculate the number of moles of produced H₂, by three different methods:

1. Using the ideal gases law (gas volume measured in the gas burette).
2. Calculating the number of moles of H⁺ consumed considering the pH change described above (Henderson−Hasselbalch's law).
3. Calculating the number of moles of H₂ by using the Faraday's law. The area under the current vs. time curve of Fig. 8(B) was obtained by integration.

In each case we obtained the values described below (average of 3 independent experiments). The total amount of charge (Q) was obtained by subtracting the blank value (-0.037 ± 0.005 A s, which did not produce gas): -0.93 ± 0.02 A s.

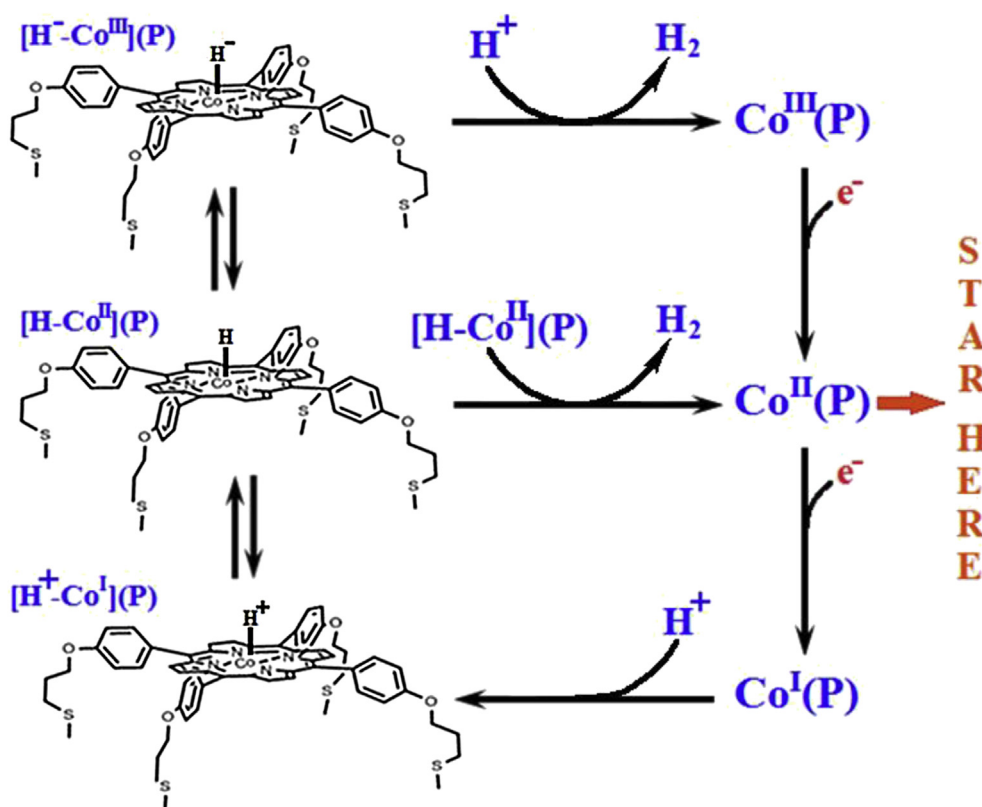- From the ideal gases law: moles of H₂ = $(8.18 \pm 0.26) \times 10^{-5}$ mol

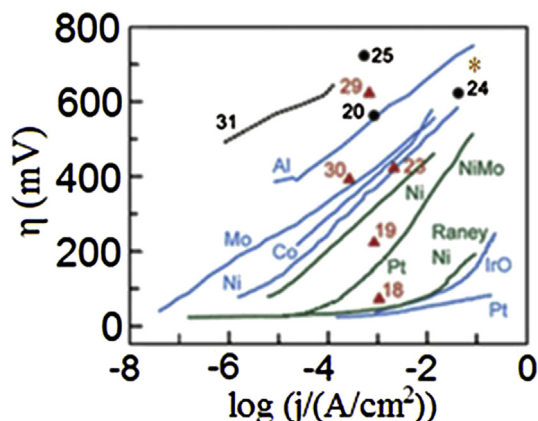**Fig. 6.** Proposed mechanism for [Co–P] catalysis of H₂ production from water.

Fig. 7. Selected data to show the activity of catalysts for HER (Hydrogen Evolution Reaction), taken from Nocera, G., et al. [48]. Polarization data for extended solids dissolved in an alkaline medium (green lines) and acidic conditions (blue solid lines). Molecular compounds evaluated in acetonitrile (red triangles) and water (circles). Orange asterisk: **[Co^{II}–P]**porphyrin deposited on gold (orange asterisk) in AcCN containing 5% water; supporting electrolyte N(Bu)$_4$PF$_6$. **24**: Co and Pt-porphyrins adsorbed onto glassy carbon in 1 M HClO$_4$ [49]; **25**: Co-phthalocyanin-electro-polymerized onto glassy carbon in phosphate buffer, pH = 2.4 [50]; other catalysts, which are not related to porphyrin-macrocycles, are described in the work by Nocera [48] and references therein. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

- By considering the pH change: moles of H$_2$ = (8.52 ± 0.89) × 10^{-5} mol
- By using the Faraday's law: moles of H$_2$ = (9.23 ± 0.96) × 10^{-5} mol

As observed, the obtained values are very close together. The average is (8.89 ± 0.96) × 10^{-5} mol. With this value we can calculate the TON (turnover number) and TOF (turnover frequency). Knowing that the electrode coating is 25% [16], and taking into account the total electrode surface (ca. 130 mm^2), the number of moles of catalyst on the electrode surface is 9.59 × 10^{-12} moles; then the values obtained are: TON = (9.27 ± 0.93) × 10^6; and TOF = (3.86 ± 0.39) × 10^3 s^{-1}. The TON and TOF numbers are very high, which shows the great efficiency and robustness of the electrode.

In Fig. 9(A), the formation of gas (bubbles) are observed around the electrode. At the end of the measurements the electrode is only partially deteriorated (note a darker coloration in Fig. 9(B)).

4. Conclusions

A TPP (tetraphenylporphyrin) derivative was attached, via sulfur covalent bonds, as a monolayer to gold and silver surface. These surfaces were used as electrodes. In the case of silver the monolayer was easily desorbed, but the modified gold electrode was found to
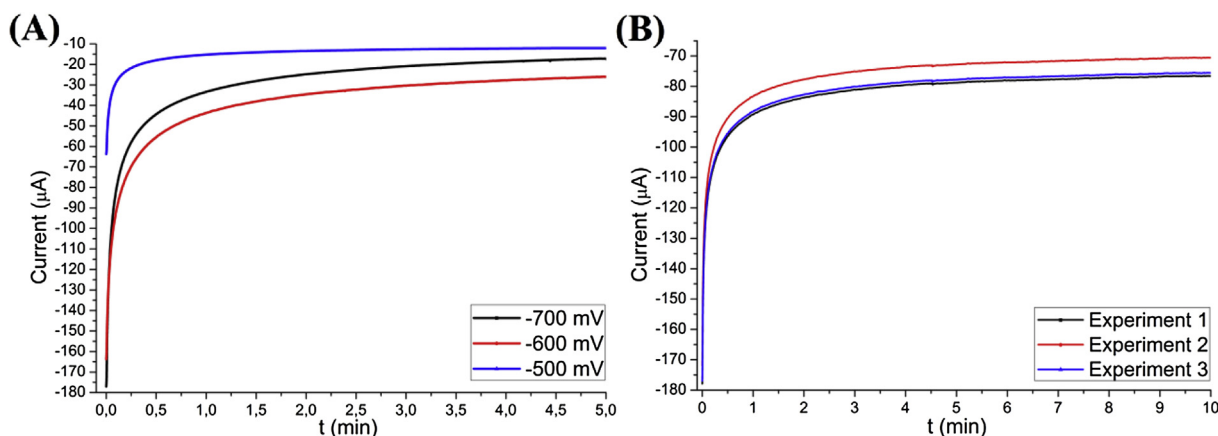

Fig. 8. Amperometric experiments carried out to determine the extent of formation of H$_2$. (A) Current vs. time behavior at different overpotential values. (B) Three independent amperometric experiments carried out at −700 mV (which is the determined overpotential value for H$_2$ production).
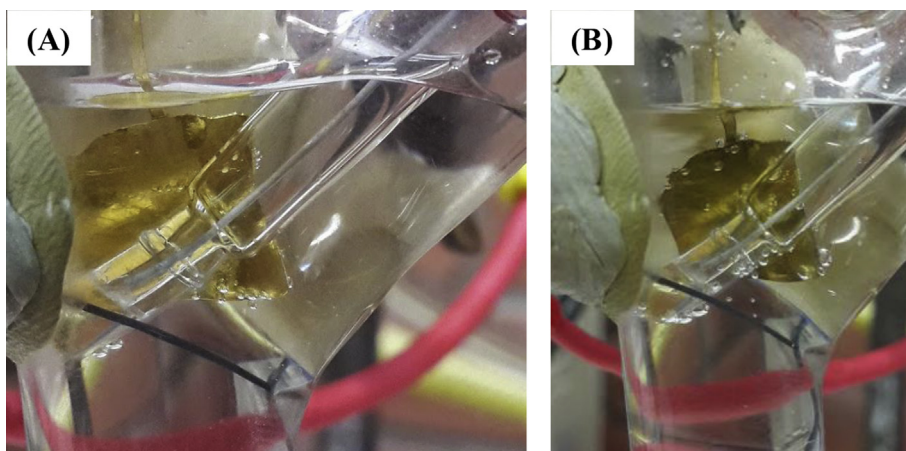

Fig. 9. Picture of the electrochemical cell with formate buffer (pH = 3), (A) at 30 min after starting the experiment and (B) at the end of all experiments (ca. 200 min).

be a strong material. Water reduction to produce hydrogen is catalyzed by this surface with high currents and at a reasonable overpotential, at not so low pH values. Formation of oxygen from water is also catalyzed by this surface, indicating that water splitting could be achieved in a controlled and flexible manner by the use of these modified gold electrodes as anodes and cathodes. Compared with the results obtained with dissolved Co porphyrins in solution by Spiro and coworkers, in our case a monolayer allows the use of only a tiny amount of material, because a small volume of diluted porphyrin solution can be utilized to modify a large number of electrodes. Moreover, since the catalyst is covalently attached to a surface, the modified electrode is a quite robust material that can be reused several times.

Acknowledgment

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.matchemphys.2015.03.065.

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