



Enhanced light-induced hydrogen evolution reaction by supramolecular systems of cobalt(II) and copper(II) octaethylporphyrins on glassy carbon electrodes



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ABSTRACT

Chemically modified glassy carbon electrodes formed by π -stacking of commercial cobalt (II) and copper (II) porphyrins have been used as stable and efficient electrocatalytic system for the hydrogen evolution reaction at pH 7.0, as reported in a previous work. In this work, it has been found that when these systems are irradiated with light of different wavelengths, their electrocatalytic responses change in terms of overpotential and photocurrent. Thus, the electroactivity of these systems towards hydrogen evolution reaction can be enhanced by irradiation at certain wavelength with no requirement of a photosensitizer. Interestingly, the largest enhancement of this reaction is observed at wavelengths corresponding to specific arrangement of porphyrins on the electrode. Cyclic voltammetry, photoelectrochemical impedance spectroscopy and UV–visible spectroscopy studies were done in order to corroborate and discuss this effect. Finally, XRD experiments allowed us to confirm the existence of highly ordered arrangement in each supramolecular system and that this is a determinant factor in the photoelectrochemical responses.

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1. Introduction

Realization of the hydrogen economy will require efficient and sustainable production of hydrogen gas. When this product is generated from a non-carbon source, it becomes an attractive clean fuel candidate for sustainable energy storage and transport [1–3]. However, the production of molecular hydrogen requires the development of efficient electrocatalysts composed of abundant and inexpensive elements – such as carbon – and that decrease the overpotential of the hydrogen evolution reaction (*her*) [4–6]. Until now, platinum is the most electroactive and electrochemically stable catalyst, making it challenging to find an appropriate substitute. Thus, a small number of efficient homogeneous catalysts have been reported for this reaction [7–9]. Aza-macrocyclic compounds, such as metalloporphyrins and metallophthalocyanines,

are especially important because of their rich redox behavior and chemical stability. Actually, these kinds of complexes have been extensively studied as electrocatalysts in solution and forming part of modified electrodes [10], where cobalt [11,12], iron [13] and rhodium [14] porphyrins have shown to be very active for electrocatalytic H₂ evolution. In this sense, their capacity to act as efficient electrocatalysts is mainly due to the combination of catalytic and redox properties of porphyrins and metal centers, which improve the electron transfer in order to reduce protons and the generation of hydrogen gas as final product. Moreover, these compounds are photochemically active due to their similarity to key dyes of natural photosynthesis, making them promising candidates from the viewpoint of photoinduced electron transfer processes, both at the molecular and supramolecular level [15]. At this point, many works have proven the effectiveness of using cobalt porphyrins to photo-induce electrochemical reactions, such as *her* and CO₂ reduction [10,16], because selective photoexcitation of these porphyrins to their first singlet excited state leads to electron transfer from the chromophore to the Co center of cobaloxime,

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which implies the formation of Co reduced species that are fundamental for H₂ production or other reduced species [17]. Thus, metalloporphyrins have the appropriate excited-state properties and stability required for H₂ production systems. However, the use of a photosensitizer is, in most of the cases, crucial to avoid charge recombination processes.

In a previous work [18], we found out that very active and efficient supramolecular systems, towards hydrogen evolution reaction, can be generated with glassy carbon electrodes covalently modified with oxidized groups (ox) and 4-aminopyridine (4AP), plus deposition of cobalt (II) and copper (II) octaethylporphyrins (Co(II)OEP, Cu(II)OEP). The method of modification and the effect of the metal center were analyzed. In this work, we have assessed the effect of irradiation at fixed wavelength on the catalytic activity of these systems. The results indicate that under irradiation they become substantially better hydrogen-evolving catalysts in aqueous solution (pH 7.0) as compared to the non-irradiated systems. The light irradiation of these systems improves the response in terms of photocurrent and overpotential towards *her*, suggesting that they are good electrocatalysts and photoelectrocatalysts, with no need of a photosensitizer since the supramolecular systems exhibit a high absorption at the used wavelengths. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and UV–visible spectroscopy were used to understand the behavior of these systems. It is a matter of great interest to explore the possibility to generate hydrogen gas from water splitting using a source of renewable energy such as solar light.

2. Experimental

2.1. Chemicals and solutions

Potassium chloride, sodium hydroxide and dichloromethane were obtained from Merck as analytical grade reagents. Argon (99.99% pure) was purchased from AGA, Chile. Metalloporphyrins (2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine cobalt (II), 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine copper (II)), 4-aminopyridine, potassium dihydrogen phosphate, disodium hydrogen phosphate, hydrochloric acid (37% w/w) and hydrogen peroxide were all purchased from Sigma-Aldrich Chile. Deionized water was obtained from a Millipore-Q system (18.2 MΩ cm).

2.2. Instrumentation

Cyclic voltammetry and electrochemical impedance spectroscopy studies were performed on a CH Instruments 750D potentiostat galvanostat. The conventional three-electrode system consisted of a glassy carbon (GC) working electrode (0.071 cm²), Ag/AgCl (3 M KCl) reference electrode, and a platinum wire counter electrode.

UV–Visible spectroscopy studies were performed by using a Specord 40 spectrophotometer.

For photoelectrochemical studies, a special cell with a quartz window, to let a better irradiation on the electrode, was used. LED lights of different wavelengths and intensities were used to irradiate the electrochemical cell (5 cm away). Specifications of LED lights used in this study are given in Table 1.

XRD experiments were performed in a PANalytical XPert Pro MPD instrument ($\lambda_{\text{Cu}} = 1.54$ nm, PIXcel 1D detector) and using GC modified electrodes (1.7 cm²).

2.3. Preparation of modified electrodes and analysis

The GC electrode was polished to a mirror finish on a felt pad using alumina slurries (3 μm). Then, it was cleaned by immersion in

Table 1

Wavelength and intensity of LED lights used in photoelectrochemical experiments.

Wavelength (nm)	LED intensity (W/m ²)
380	150
395	800
420	250
495	350
520	150
560	200
610	50
620	150
660	650

an ultrasonic bath for 60 s, and finally stabilized by cycling the potential between −0.7 V and 0.7 V in a solution of 0.1 M NaOH under Ar atmosphere.

Covalently modified electrodes were obtained as reported previously using NaOH and 4AP [19,20]. Then, they were submerged in a 0.2 mM solution of metalloporphyrin, M-OEP (M = Co(II), Cu(II)) dissolved in CH₂Cl₂, for 20 min at room temperature (In) and for 60 min under reflux (R). The electrodes were then dried at room temperature for 1 min.

All the modified electrodes were analyzed in a phosphate buffer solution (H₂PO₄[−]/HPO₄^{2−} 0.066 mol L^{−1} purged with Ar) by cycling the potential between 0.4 V and −1.4 V. EIS studies were performed at a fixed potential of −1.0 V in the frequency range of 1 Hz–100,000 Hz in the same phosphate buffer solution. Also, the modified electrodes were analyzed by using XRD as technique.

The glass substrates (G) were pre-cleaned by treatment in 30% v/v NaOH and 30% v/v H₂O₂/water (1:1:4) with the aim of generate functionalized glass (G-O[−]), followed by piranha solution, HCl 30% v/v and H₂O₂/water (1:1:4) (G-OH) [21]. The glass beads were removed and rinsed with Millipore-Q water and dried under vacuum at 50 °C.

3. Results and discussion

3.1. Voltammetric measurements

In a previous work [18], we have shown that it is possible to generate supramolecular systems onto glassy carbon electrodes, which are highly active towards *her*. After an exhaustive study, the best systems were identified as GC + 4AP + Co(II)OEP, GC ox + Cu(II)OEP and GC + Cu(II)OEP, which were obtained by reflux (Scheme 1).

In this study, the effect of light on the activity of these systems towards *her* is analyzed. Under irradiation at different wavelengths it is observed that the current density increases and the overpotentials are shifted to positive potentials. The magnitude of these changes depend on the used wavelength (see Fig. S1, Supporting Information), and therefore to identify the most efficient photoelectrocatalytic system the photocurrents measured at a given reduction overpotential were compared. In Table 2 are given the used wavelengths in a decreasing order of light-induced response for each system, measured in terms of overpotential. Thus, the highest photoelectroactivity is directly related to the lowest onset overpotential for hydrogen evolution.

These results suggest that in presence of light there is a diminution on the energy band gap that is necessary to reduce protons and produce hydrogen. It has been proposed that the charge transfer interaction between the metal and the ligand π system stabilize the redox pair. In this sense, the presence of a delocalized π system in the porphyrin macrocycle can help to stabilize the low oxidation states of metal centers, due to partial delocalization of the

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