

Supported bimetallic polymers of porphyrins as new heterogeneous catalyst

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Abstract

New heterogeneous catalytic systems of mono and bimetallic polymeric porphyrinic structures confined to Au surface are described. The solid materials were characterized by AFM, SEM and EDS/EDX techniques. The polymeric films have been deposited by consecutive voltammetric cycles. The appearance of a peak at 380 mV (vs. Ag/AgCl), is only observed in the first cathodic scan of the bimetallic structures and was attributed to Cu(III)/Cu(II) reduction in polyFeCuPP. In all the cases studied, the bimetallic structures were up to 3.5 times more efficient catalyst than the corresponding monometallic.

PolyCoCuPP is intrinsically weaker than polyFeCuPP. Nevertheless, the mass deposited is significantly higher (80%). For this reason, poly-CoCuPP is considered the best catalyst under practical considerations.

The use of a solid catalyst with a small amount of H₂O₂, in aqueous solution, makes this oxidation an environmentally benign chemical process.
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1. Introduction

There is much concern about promoting innovative chemical technologies to reduce or eliminate the application or generation of hazardous substances in the design, manufacture, and use of chemical products [1]. Without any doubt, the hydrogen peroxide as oxidant has made an appreciable contribution to a cleaner chemical industry where it plays an important role, especially in selective oxidations [2].

The aqueous H₂O₂ is an excellent green oxygen donor, since it only generates water as a by-product. In general, hydrogen peroxide is not able to oxidize organic compounds by itself; therefore introduction of an inorganic or organic catalyst for active oxygen transfer is a necessity in the oxidation system.

Metalloporphyrins have been extensively explored as biomimetic catalysts, following the action of cytochrome P450. They lead to oxygenation reactions mediated by high-valent

metal–oxo porphyrin complexes [3]. The accepted mechanism describes an intermediate hypervalent metal–oxo specie (M⁵⁺=O), that can be formed with certain transition metals complexes of porphyrins (Mn(III), Fe(III) and Co(III)) [3].

Most work in this area has been done using iron and manganese porphyrins, containing electronwithdrawing meso-substituents to avoid degradation of aromatic porphyrin ring [4].

In our work with polymeric metalloporphyrins we observed that the supramolecular structure, resulting from electropolymerization of metalloprotoporphyrin IX, was stable enough to catalyse *cis*-stilbene epoxidation [5]. In this early experiment, we could observe that the polymer matrix was able to prevent metalloporphyrins degradation and controlled the access of substrate molecules to the reactive center.

More recently, we studied the amperometric response of modified electrodes resulting of the combination of different films of metalloporphyrins. The electrochemically active structures showed high electron transfer capability and stability [6]. These results are in line with the synergistic catalytic effect observed in heterobimetallic systems, wherein

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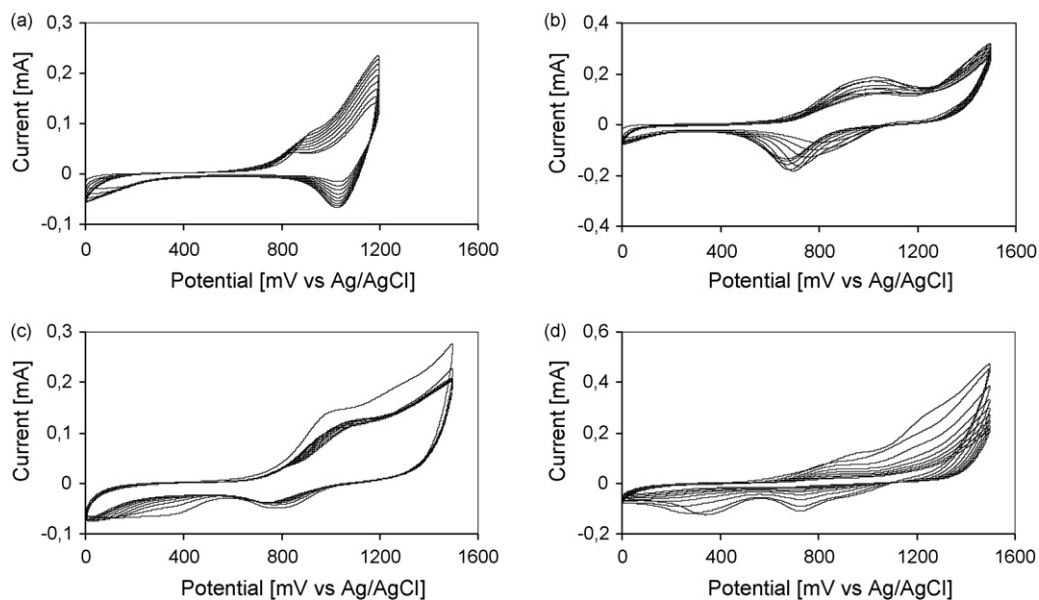


Fig. 1. Voltammograms obtained during electropolymerization at 50 mV s^{-1} of (a) polyFePP; (b) polyCuPP; (c) polyFe–polyCuPP; (d) copolymerization of FePP and CuPP. Linear sweep 0.00 to +1.50 V vs. Ag/AgCl⁻, for all monomers except FePP (0.00 to +1.20 V vs. Ag/AgCl).

a mixture of metal complexes was demonstrated to be more active than either of the complexes when used separately [7,8].

With these ideas in mind we used the electropolymerization technique to build up multilayered heterobimetallic porphyrinic structures over Au surface and explored them as heterogeneous catalyst. The monomers could be electropolymerized in a controlled manner, leading to well-defined supported catalysts.

Considering that heterogeneous catalyst have many advantages over the homogeneous counterparts, especially as environmentally benign chemical process, we explored the bimetallic supported catalyst as activators of H_2O_2 .

In this paper we report a heterogeneous catalytic study of bimetallic polymer structures confined to Au surfaces. As far as we know, this is the first catalytic study using bimetallic polymeric porphyrins structures. The peroxidase versus catalase action of these systems is discussed.

2. Experimental

2.1. Reagents

Metalloprotoporphyrin complexes were prepared according to standard procedure [9]. Dichloromethane (Merck), and tetrabutylammonium perchlorate (TBAP) (Sigma) were analytical grade and used as received. Metalloprotoporphyrin solutions of 0.25 mg mL^{-1} concentration (unless otherwise noted) were prepared with CH_2Cl_2 and 0.1 M of TBAP.

2.2. Deposition of metalloprotoporphyrin films

Electropolymerization of metalloprotoporphyrins were carried out in 0.1 M TBAP/ CH_2Cl_2 by potential sweep between 0.00 and +1.50 V (vs. Ag|AgCl) at 0.05 V s^{-1} , four cycles; for all the mono and bimetallic polymers except FePP (0.00 to +1.2 V).

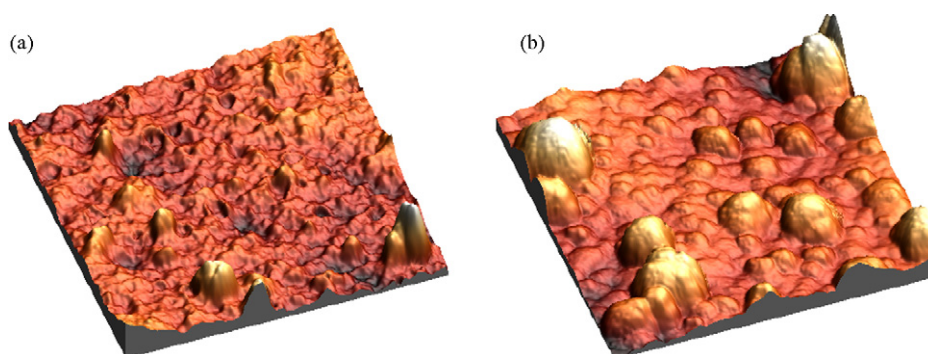


Fig. 2. AFM images of Au surfaces covered with (a) polyCuPP over polyFePP (polyFeCuPP) (b) copolymerized FePP and CuPP.

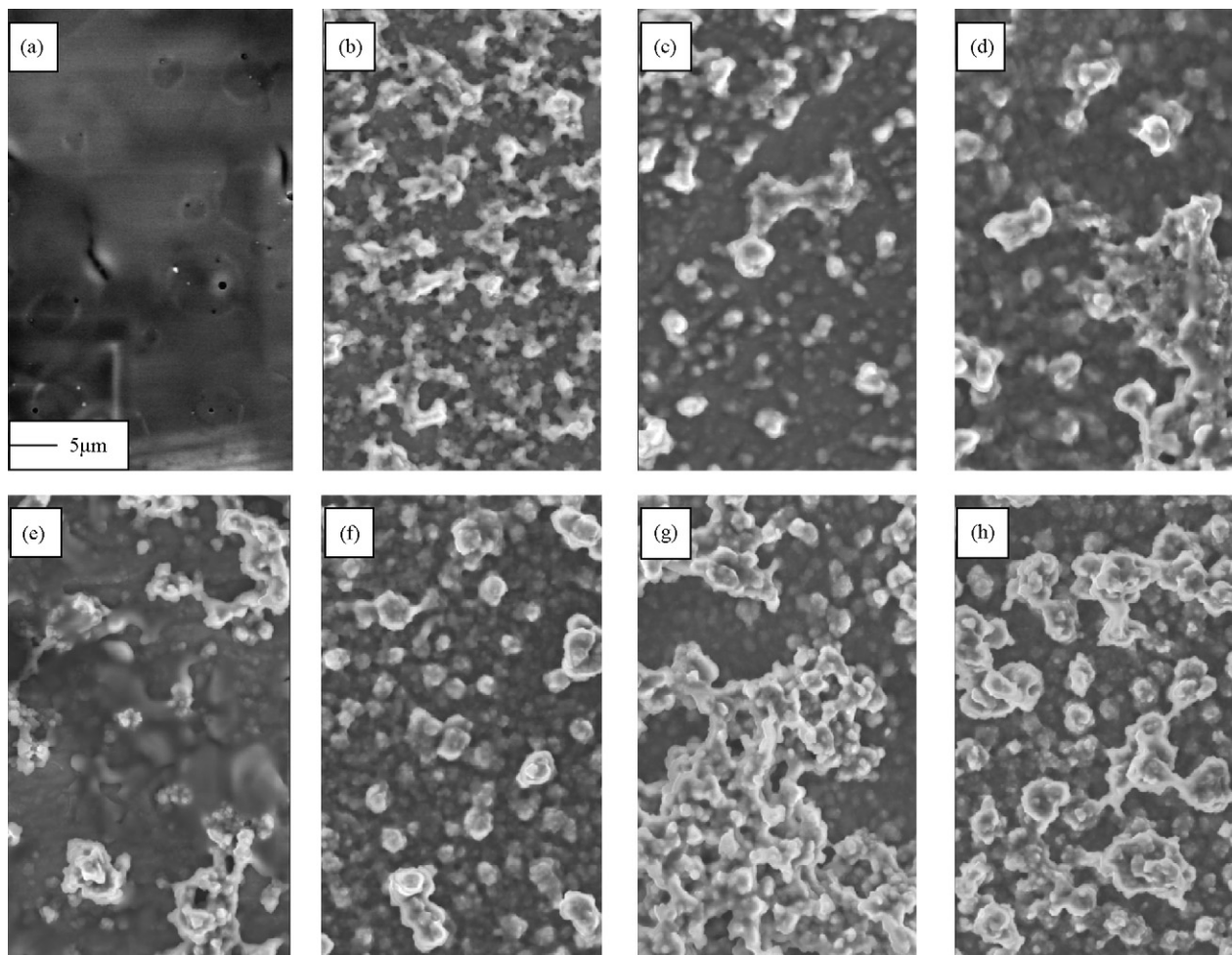


Fig. 3. SEM images (magnification 5000 \times) of different mono and bimetallic polymers deposited over Au surface: (a) polyFePP; (b) polyCuPP; (c) polyFeCuPPIX; (d) polyFeNiPPIX; (e) polyCoPPIX; (f) polyNiPPIX; (g) polyCoCuPPIX; (h) polyCoNiPPIX.

2.3. Catalytic experiments

The catalytic activity was explored through the dye formation reaction between 4-aminoantipyrene and phenol in presence of H₂O₂. In a typical reaction the solid catalyst was added to 1.5 ml of mixture (v/v) of phenol (0.1 mol/L), 4-aminoantipyrene (1.5×10^{-3} mol/L) and the phosphate buffer solution at pH 7.0 (0.10 M). Variable hydrogen peroxide concentration (1–200 mM) was added and stirred. The absorbance of the solution was then measured at 505 nm (λ_{\max} of the quinoid dye). A HP8452 diode array spectrophotometer and a quartz crystal cell were used to obtain UV spectra. The catalytic activity of the catalysts was then evaluated by comparing the absorbance of the quinoid dye formed.

2.4. Apparatus

Cyclic voltammeteries (VCs) were performed with a purpose built potentiostat (microprocessor controlled), with digital signal generator for implementation of different electrochemical techniques. Au working electrode (0.36 cm² area), a Ag/AgCl reference electrode (BAS) and a platinum wire auxiliary

electrode were used for voltammetric experiments of electrodeposition.

Nanoscope IIIa-Quadrex, Digital Veeco (AFM) was used for AFM experiments, performed in tapping mode with a resonance frequency of 300 kHz previous nitrogen bubbling. The tips were commercially available Si tips (40 N/m) supplied by Digital Instruments.

The scanning electron micrographs of the polymers were obtained using a Zeiss DSM 982 GEMINI SEM with Field Emission Gun (FEG), operated at 5 kV. The elemental composition of metals in different parts of the porphyrins films was determined by Energy Dispersive X-ray Analysis (EDS INCA ENERGY, Oxford Instruments) with acceleration voltage of 20 kV.

3. Results

We have studied the catalytic activity of hydrogen peroxide reduction of new heterobimetallic polymeric porphyrinic structures confined onto Au surfaces. They have been prepared by electropolymerization of different metallic complexes of protoporphyrin IX dimethyl ester (PPIXDME). The Fe(III) and Cu(II) complexes of protoporphyrin IX dimethyl ester, named FePP and CuPP, were mostly studied due to their importance

Table 1a
Elemental composition of metals in different parts of the porphyrins films for polyCoNiPP

Element	Weight%	Atomic%
C K	81.49	88.92
OK	13.50	9.36
Cl K	3.40	1.24
Co K	0.96	0.29
Ni K	0.65	0.19
Total	100	

in biologic systems. Nevertheless, other transition metal complexes were also explored (Co, Ni, Zn). The monomers were electropolymerized and deposited in different order over the electrode surface.

As monometallic polymers, we studied polyFePP, polyCuPP, polyCoPP and polyNiPP. The bimetallic structure, were either polyFePP-based, when a second polymer was deposited over a film of polyFePP: polyFeCuPP and polyFeNiPP; or polyCoPP-based (polyCoCuPP and polyCoNiPP).

Fig. 1a and b show voltammograms obtained during the electropolymerization process, corresponding to FePP and CuPP monomers, respectively. While Fig. 1c and d shows the electrochemical formation of the bimetallic polymers. The former corresponds to the electrodeposition of CuPP over a very thin film of polyFePP and Fig. 1d is obtained during copolymerization of both CuPP and FePP monomers. All of them showed increasing anodic and cathodic peak currents on successive scans, indicating that the electrodeposition takes place at positive potential where the radical cation is formed [10]. It is noteworthy that the appearance of a peak at 380 mV (Fig. 1c and d) is observed in the first cathodic scan of the bimetallic polymer formation. This peak could be attributed to Cu(III)/Cu(II) reduction [11,12], assuming that the presence of FePP and the extremely oxidative potential promote the formation of the unstable Cu(III)

Table 1b
Elemental composition of metals in different parts of the porphyrins films for polyCoCuPP

Element	Weight%	Atomic%
C K	78.84	85.92
OK	14.93	12.22
Cl K	3.42	1.26
Co K	1.33	0.30
Cu K	1.47	0.30
Total	100	

specie, in the first voltammetry. At this point we can conclude that metals are present in their oxidized form in these polymers, which is the most favourable for H₂O₂ binding [13].

Fig. 2a and b is AFM images of Au surfaces covered with (a) a consecutive deposit of polyCuPP over polyFePP (polyFeCuPP) and (b) copolymerized FePP and CuPP. AFM topography images of the copolymerized structure showed a major surface covering than the polyFeCuPP. Nevertheless, the second structure resulted to be the most efficient for hydrogen peroxide reduction, exhibiting the highest initial activity and suggesting the need of a sequential deposit of films to assure the bimetallic centers interaction. We have obtained SEM images of different mono and bimetallic polymers deposited over Au surface: (a) polyFePP; (b) polyCuPP; (c) polyFeCuPP; (d) polyFeNiPP; (e) polyCoPP; (f) polyNiPP; (g) polyCoCuPP; (h) polyCoNiPP. Although the growth processes are virtually identical, the morphologies of the polymerized structures are quite different.

The FePP film shows a small surface coverage (Fig. 3a) that could be attributed to the tendency, of the oxidized monomer, to evolve to the μ -oxo-bridged dimers.

The images of monometallic polyCuPP (Fig. 3b) and polyNiPP (Fig. 3f) showed more homogeneous films, consistent with previous EQCM experiments [14]. When the bimetallic structure was built over polyFePP deposited onto Au,

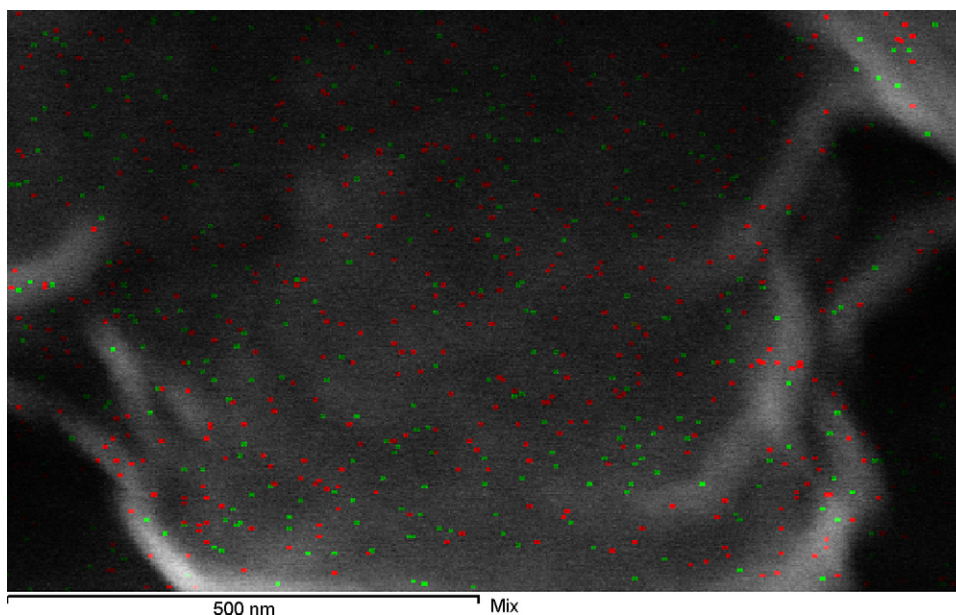


Fig. 4. EDS mapping of polyNiPP (green dots) deposited over polyCoPP (red dots).

Table 2a

Kinetic behaviour for mono and bimetallic polymeric catalyst after 60 min of catalytic reaction; pH 7.0; (1.5 mM) 4-aminoantipyrine; (100 mM) phenol; at different concentrations of H₂O₂

Catalyst	Surface concentration ^a ($\times 10^{-8}$ mol cm ⁻²)	Concentration of product [$\times 10^{-6}$ M] at 60 min				
		[H ₂ O ₂] = 1 mM	[H ₂ O ₂] = 3 mM	[H ₂ O ₂] = 10 mM	[H ₂ O ₂] = 50 mM	[H ₂ O ₂] = 200 mM
PolyNiPP	1.59	1.44	2.69	3.21	–	–
PolyCuPP	1.40	1.29	1.69	1.69	11.1	12.7
PolyFePP	0.282	4.37	7.06	7.68	19.6	15.6
PolyCoPP	1.74	11.4	18.3	20.2	–	–
PolyFeCuPP	0.303	7.70	13.1	14.7	24.7	17.8
PolyCoCuPP	1.82	20.1	34.1	37.5	–	–
PolyCoNiPP	1.97	17.2	27.3	32.8	–	–

^a Obtained from EQCM experiments.

images showed heterogeneous polymer distribution. It is interesting to observe that the structure of the first immobilized film, establishes the catalyst morphology (Fig. 3c and d). In an independent experiment, polyCo(III)PP was initially electropolymerized onto Au. A higher mass of porphyrin was observed in the monometallic structure (Fig. 3e) and more homogeneous bimetallic catalysts were obtained when polyCuPP and polyNiPP were generated over polyCoPP (Fig. 3g and h, respectively).

We performed energy dispersive X-ray microanalysis (EDAX/EDS) spectra of the catalyst based on polyCoPP structure exclusively. The elemental composition of metals in different parts of the porphyrins films was determined by energy dispersive X-ray analysis. In the case of polyCoNiPP, two-thirds of Ni relative to Co was obtained (Fig. 5a and Table 1a). On the other hand, polyCoCuPP showed an excellent correlation between the amount of CoPP and CuPP deposited (Fig. 5b and Table 1b).

To get an insight into the metal composition, since the sensitivity of X-ray microanalysis is not good enough to detect polyFePP in such small amount (Fig. 4), the covering material of 10 modified electrodes of both polyFePP and polyFeCuPP films, were separated from the Au surface and collected for atomic absorption spectroscopic analysis. A 6.5% P/P of Fe was obtained in polyFePP, whereas 10% P/P of Cu:Fe (3:2) was found in polyFeCuPP. These results are in agreement with previous EQCM experiments [14].

3.1. Catalysis experiments

It is well known that metalloporphyrins are able to catalyse the oxidation of phenolic compounds in the presence of hydrogen peroxide through a catalytic cycle similar to the peroxidase enzymes [15]. In the present study, we have

Table 2b

Initial reaction rate at the lower H₂O₂ concentration, normalized by Γ

Catalyst	(Γ) Surface concentration ^a ($\times 10^{-8}$ mol cm ⁻²) of catalyst	Initial rate of product formation (M seg ⁻¹) [H ₂ O ₂] = 1 mM	Initial reaction rate normalized by Γ at mol seg ⁻¹ cm ² molcat ⁻¹ [H ₂ O ₂] = 1 mM ($V_i \Gamma^{-1}$)
PolyFeCuPP	0.303	1.49×10^{-8}	7.37×10^{-3}
PolyCoCuPP	1.82	3.88×10^{-8}	3.20×10^{-3}

^a Obtained from EQCM experiments.

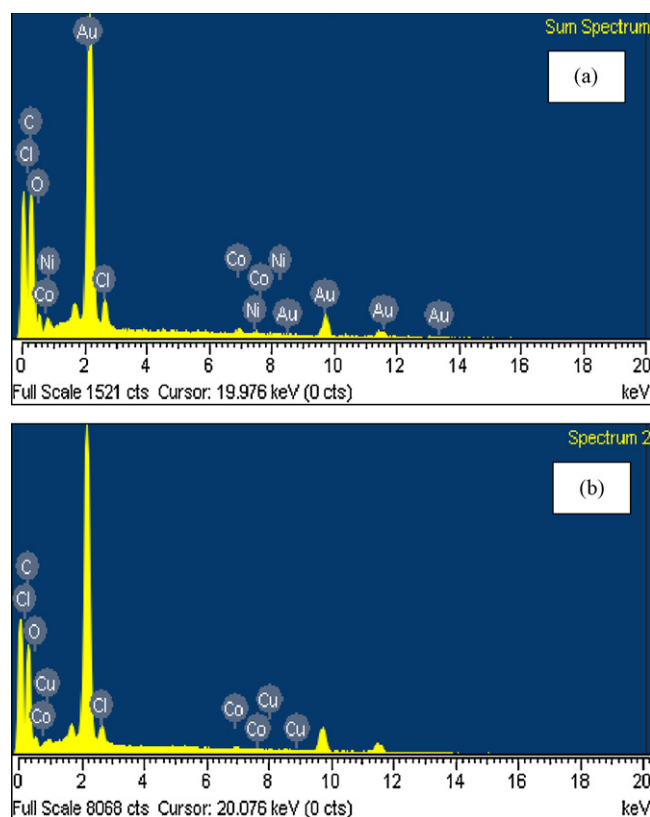


Fig. 5. Energy dispersive X-ray analysis exploring the elemental composition of metals in different parts of the porphyrins films of polyNiPP deposited over polyCoPP (a) and polyCuPP deposited over polyCoPP (b).

selected the oxidation of phenol and the following condensation with 4-amino-antipyrine (1), as test reaction of the supported catalysts described. Progress of this reaction could be easily monitored by tracing the quinoid type dye (2) formation

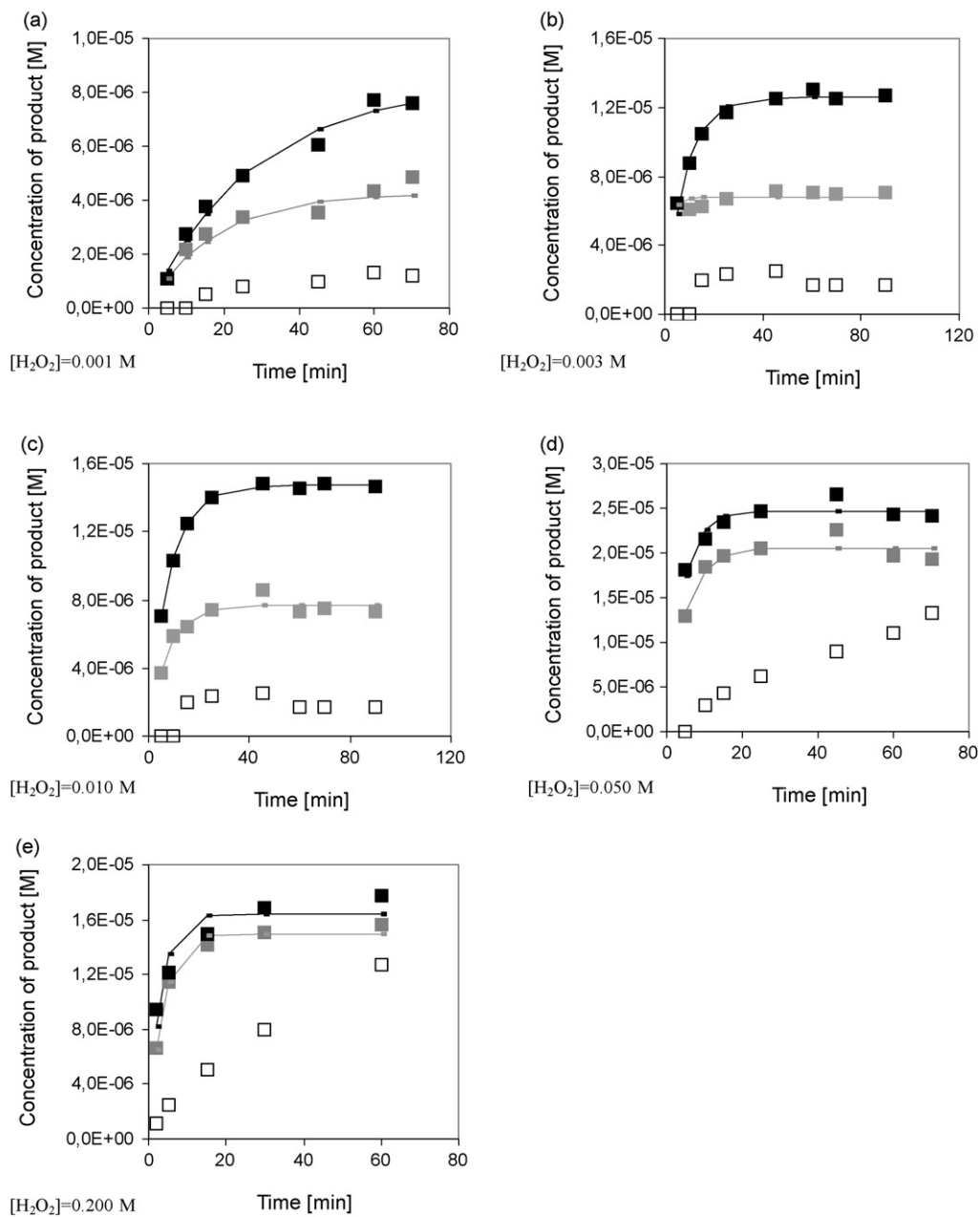
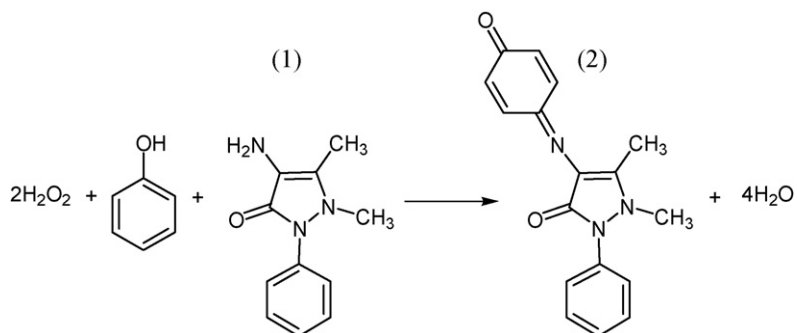


Fig. 6. Kinetics curves at different H_2O_2 content (a) 0.001 M, (b) 0.003 M, (c) 0.010 M, (d) 0.050, (e) 0.20 M; (■) polyFeCuPP; (■) polyFePP and (□) polyCuPP.



Scheme 1.

Table 3
The ratio $k_1/(k_1 + k_2)$ for mono and bimetallic catalyst at different concentration of H_2O_2

$[H_2O_2]$ (M)	PolyFePP $k_1/(k_1 + k_2)$	PolyFeCuPP $k_1/(k_1 + k_2)$
0.001	4.24	14.61
0.003	1.99	4.216
0.010	0.766	1.469
0.050	0.411	0.496
0.200	0.075	0.082

(Scheme 1) [16], which has an intense absorption band at 505 nm ($\epsilon = 8000 \text{ M}^{-1} \text{ cm}^{-1}$). This fact allowed us to detect the reaction product with an exceptional detection limit.

Fig. 6 shows the kinetic behaviour of the bimetallic polyFeCuPP and the corresponding monometallic polyFePP and polyCuPP, prepared by the deposit of the polymers onto Au surface. We also studied the reactivity of the copolymer, no dye formation was observed in this last case, suggesting the need of certain geometric disposition for the catalytic action.

Steady-state kinetics of phenol oxidation was carried out 505 nm. The curves were obtained at different concentrations of hydrogen peroxide. Fig. 6 shows, there are significant differences in the catalytic action of mono and bimetallic structures, especially at lower concentrations of H_2O_2 . Table 2a summarizes these results including all the films studied in this paper. It is easy to observe the uncontroversially fact that all the bimetallic systems resulted in a more efficient catalyst than the individual components, indicating a synergic effect between metal centers. Also, it must be noticed that the polyCoPP-based bimetallic structures (polyCoCuPP and polyCoNiPP) lead to higher dye production than the polyFePP based ones. Nevertheless, polyFeCuPP resulted the best catalyst when the efficiency was expressed as initial rate reaction, normalized by surface concentration of the catalyst ($V_i \Gamma^{-1}$) (Table 2b).

It is very well known that oxidative process with H_2O_2 involving metalloporphyrins can follow either a *peroxidase type* or *catalase type* mechanism of action, resembling the different hemoproteins in nature. Both of them require a high-valent intermediate $M^{5+} = O$, that can evolve to the resting form $M(III)$ porphyrin by oxidation of a high electronic specie (*peroxidase type*) or by releasing O_2 and water (*catalase type*). These two mechanisms are competitive and have different requirements to occur [4,6]. Each of them has their own constant rate, k_1 and k_2 , respectively. Considering a similar behaviour in our catalytic system, we explored the fitting of data in Fig. 6 to Eq. (1), containing two rate constants, related to the competitive reactions described.

$$[\text{dye}] = \frac{k_1 [H_2O_2]}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t}) \quad (1)$$

The k_1 and k_2 values obtained from Eq. (1) at variable H_2O_2 concentration showed excellent regression coefficients for all cases (R^2 higher than 0.98). As an idea of the catalytic efficiency per microgram of catalyst we calculated the ratio $k_1/(k_1 + k_2)$. Table 3 shows the fraction of peroxidase type mechanism, for the mono and bimetallic polyFePP and polyFeCuPP at different concentration of H_2O_2 . It easy to notice, that bimetallic

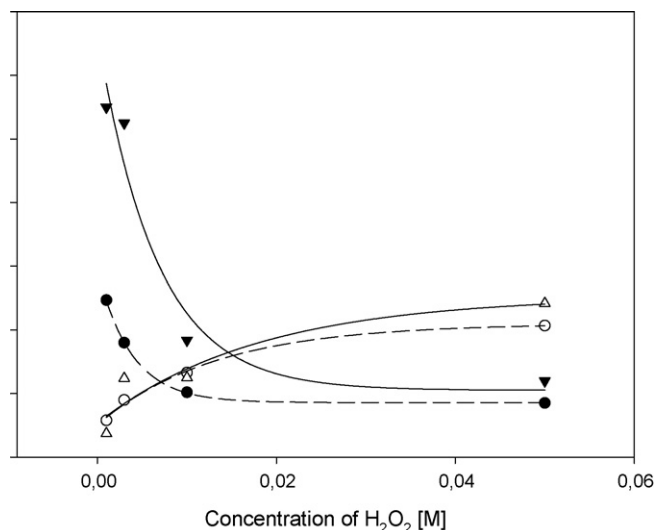


Fig. 7. k_1 and k_2 (calculated from Eq. (1)) vs. concentration of H_2O_2 ; polyFeCuPP (full line) and polyFePP (dashed line). PolyFeCuPP (\blacktriangledown) k_1 and (\triangle) k_2 . PolyFePP (\bullet) k_1 and (\circ) k_2 .

systems showed significant higher relative k_1 values at low concentration of H_2O_2 leading to dye formation. Further, at $1 \times 10^{-3} \text{ M}$ the bimetallic system is 3.5 times more efficient than the monometallic. The differences decrease with increasing concentrations of H_2O_2 , at $3 \times 10^{-3} \text{ M}$ is two times. At concentrations higher than 50 mM a notable diminution in peroxidase type reaction is observed and mono polyFePP and bimetallic polyFeCuPP catalytic process are essentially the same. This result is completely in line with previous reports [17], describing that high concentration of hydrogen peroxide would preferentially lead to the catalase path, with no significant degradation of the polymer. This latest statement is supported in the observation that when the electrodes were re-used with 50 mM H_2O_2 , only less than 3–4% of the activity was lost.

Fig. 7 shows the variation of k_1 and k_2 with H_2O_2 concentration for mono and bimetallic systems. The decreasing curves (\bullet) and (\blacktriangledown), corresponds to k_1 variation and the other two (\triangle) and (\circ) give a picture of k_2 variation. It is interesting to notice that k_2 (catalase action) is pretty similar for mono and bimetallic systems, while peroxidase (k_1) behaviour is significantly different at low concentration of hydrogen peroxide, getting closer as concentration increases.

4. Conclusions

The bimetallic systems resulted more efficient catalyst than the corresponding monometallic. PolyCoPP-based structures showed better performance, in a practical point of view, than the polyFePP counterparts. Even though polyCoCuPP is intrinsically a weaker catalyst than polyFeCuPP, the mass of polyFeCuPP deposited is 80% lower than the corresponding to polyCoCuPP.

The heterogeneous catalysts reported result an excellent environmental option since they required low concentration of H_2O_2 and aqueous solution.

Nanoparticles of Au will be modified with these structures in order to increase the surface area and the catalytic efficiency.

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