

The electrocatalytic reactions of adenine, guanine, H₂O, H₂O₂, N₂H₄, and L-cysteine catalyzed by poly(Ni(4-TMPyP)) film-modified electrodes

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Received: 1 June 2006 / Revised: 21 June 2006 / Accepted: 16 July 2006 / Published online: 11 October 2006
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Abstract Electrochemical preparation of poly(nickel tetrakis(*N*-methyl-4-pyridyl)porphyrin) tetratosylate (poly-Ni(4-TMPyP)) produces stable and electrochemically active films in strong and weak basic aqueous solutions. These films were produced on glassy carbon and gold electrodes. The electrochemical quartz crystal microbalance and cyclic voltammetry were used to study the in situ growth of poly(Ni(4-TMPyP)) films. The electrochemical properties of poly(Ni(4-TMPyP)) films indicate that the redox process was confined in to the immobilized film. The electrochemical quartz crystal microbalance results showed an ion exchange reaction for the redox couple. The polymer films showed one new redox couple when transferred to strong and weak basic aqueous solutions and the formal potential was found to be pH dependent. The electrocatalytic oxidation of H₂O by a nickel tetrakis(*N*-methyl-4-pyridyl) porphyrin film-modified electrode was also performed. The mechanism of oxygen evolution was determined by cyclic voltammetry, chronoamperometry and rotating ring disc electrode methods. The oxygen evolution was determined by a bicatalyst system using hemoglobin, and iron tetrakis(*N*-methyl-2-pyridyl)porphyrin as catalyst to detect the oxygen by electrocatalytic reduction. The electrocatalytic oxidations of adenine, guanine, H₂O₂, N₂H₄, NH₂OH, and L-cysteine by the film-modified electrode obtained from water-soluble nickel porphyrin were also investigated.

Keywords Nickel porphyrin · Adenine · Electrocatalysis · Film-modified electrode · Bicatalyst

Introduction

The electrochemical formation of film-modified electrode can be controlled by consecutive cyclic voltammetry, which makes a fine synthetic film. The increase of peak current redox couple of the film indicates film formation.

Generally, the film formation processes may involve oxidation and/or reduction. Chemically film-modified electrodes of polymeric porphyrins can be used in molecular devices combined with electrochemistry [1]. Electrodes modified with the conducting or redox polymer films have many applications [2–4]. The film-modified electrodes are widely used in the fields of electroanalysis and electrocatalysis [5–11], in bioinorganic chemistry, as chemical biosensors, and as mimic enzymatic systems [12]. Chemically modified electrodes [13, 14] show interesting film microstructure and chemical properties and may also be useful for electronic devices, chemical and biosensors, and for performing electrocatalytic reactions.

Immobilization of metalloporphyrins in electropolymerized films [1] and film-modified electrodes are interesting investigation in chemistry and biology. The electrochemical deposition conditions can be carefully controlled and leads to the formation of a conducting polymer on the electrode surface. The electrodeposition of nonmetal porphyrins [1, 15, 16] and metal porphyrins [17–21] has been investigated though most of the electrodeposition media used were nonaqueous solutions. The electrodeposition of stable metal

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porphyrin films in aqueous solution was used to perform electrocatalytic reactions in aqueous solutions. These reactions are concerned with analytical applications of electrocatalytic measurements, and with the electrochemical oxidation or reduction of electroactive compounds.

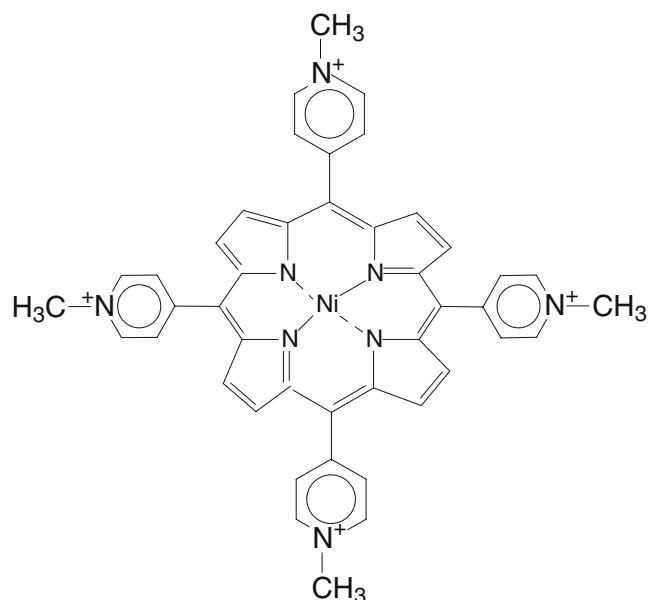
Nickel porphyrins [22–26] and nickel complexes [27–30] were used to formation of a conducting polymer. Nickel complexes have been reported as electrocatalysts for the reduction of O_2 [31]. The oxidation of water in to dioxygen is catalyzed by an oxygen-evolving complex in photosynthesis, which is one of the most important and fundamental chemical processes in nature [32–37].

From the electrocatalytic activity measurement, the results are concerned with analytical applications and with the electrochemical transfer activity toward the analysis of scarcely electroactive compounds. Using the modified electrodes, the electrochemical methods for the determination of guanine and adenine were performed. The sensitive and direct electrochemical technique for the measurement of native DNA was developed. The electrochemistry of inorganic nitrogen-containing compounds is interesting where hydrazine and hydroxylamine are the desired products of reduction process.

This paper explains the formation of electrodes modified by Ni(4-TMPyP) films (Scheme 1). The electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry were used to study the in situ growth of Ni(4-TMPyP) immobilized films. The EQCM results showed an ion exchange reaction for the redox couple. The electrochemical properties of these films and the electrocatalytic oxidation properties of adenine, guanine, H_2O , H_2O_2 , N_2H_4 , NH_2OH , and L-cysteine by them are discussed. A bicatalyst system consists of Ni(4-TMPyP) film and hemoglobin or Fe(2-TMPyP) in solution for H_2O oxidation and product determination is also discussed. The films showed one new redox couple, which was to be pH-dependent when transferred to buffer aqueous solutions. A typical amperometric ($i-t$) experiments of reduction of H_2O_2 (and the product O_2) and N_2H_4 using rotating ring-disk electrochemical (RRDE) experiments or rotating disk electrochemical (RDE) experiments were performed in a well-stirred solution by keeping the electrode potential constant (disc and ring) for 19 sequential addition of H_2O_2 and N_2H_4 . Simultaneous determination of adenine and guanine at the Ni(4-TMPyP)-modified electrode was also performed.

Experimental

Electrochemistry was performed with a Bioanalytical system (BAS) (West Lafayette, IN, USA) Model CV-50W and CHI-400 (CH Instruments) potentiostats. Cyclic



Scheme 1 Structure of Ni(4-TMPyP)

voltammetry was conducted with the use of a three-electrode cell. A BAS glassy carbon electrode (0.07 cm^2) was used as the working electrode. The glassy carbon electrode were polished with $0.05\text{ }\mu\text{m}$ alumina on Buehler felt pads and ultrasonicated for 1 min. The auxiliary compartment, which contained a platinum wire was separated by a medium-size glass frit. All cell potentials were measured with respect to an $Ag|AgCl|KCl(\text{sat})$ reference electrode or a $Hg/Hg_2Cl_2/\text{electrode KCl}$ (saturated solution) reference electrode.

RRDE experiments were performed using a Pine Instrument electrode in conjunction with a CH Instruments CHI-750 potentiostat connected to an AFMSRX analytical rotator. The RDE electrode consisted of a glassy carbon disk electrode and a glassy carbon (or platinum) ring electrode.

The working electrode for the EQCM measurements was an 8 MHz AT-cut quartz crystal with gold electrodes. The diameter of the quartz crystal was 13.7 mm, whereas the diameter of the gold electrode was 5 mm.

Solutions were deoxygenated by purging with prepurified nitrogen gas. The bovine hemoglobin (Hb) was bought from Sigma. The Ni(4-TMPyP) was purchased from Porphyrin Products (Logan, UT, USA). Aqueous electrolytes were prepared with doubly distilled deionized water. Buffer solutions were prepared from H_2SO_4 , KHP (potassium hydrogen phthalate), sodium acetate, sodium dihydrogen phosphate, TRIS, sodium carbonate, and KOH for the pH range 0–14.

The electrochemical formation of the (Ni(4-TMPyP)) films were performed by continuous cycling of the

potential of the working electrode in a defined potential range in a suitable aqueous solution containing Ni(4-TMPyP).

Results and discussion

Electrochemical deposition of poly(Ni(4-TMPyP)) in aqueous solutions

The electrochemical formation of poly(Ni(4-TMPyP)) films from aqueous solution containing 1×10^{-4} M Ni(4-TMPyP) on a glassy carbon electrode was performed using consecutive cyclic voltammetry between suitable potential range of 0.5 and 1.1 V in aqueous solution with pH 10 (see Fig. 1a). A broad peak appeared at 0.98 V during the first scan due to the oxidation of porphyrinic ring of monomer. On reverse scans, a well-defined redox couple was observed with formal potential at $E^{\circ'} = 0.75$ V. The amplitude of this redox couple was found to increase with increasing of scan number which indicates that a Ni(4-TMPyP) film was formed on the GC surface. Bedioui et al. [38] reported a similar type of result for the same monomer in alkaline solution. They also reported about the electrochemical and spectrochemical behavior of poly(Ni(4-TMPyP)) film in basic media. They have also reported that the redox couple appeared with $E^{\circ'} = 0.75$ V corresponded to Ni(II)(4-TMPyP)/Ni(III)(4-TMPyP) redox reaction of Ni(4-TMPyP) film. Beyond the potential 0.95 V, Ni(III)(4-TMPyP) film could oxidized to Ni(IV)(4-TMPyP) or Ni(V)(4-TMPyP) in alkaline condition [25, 28, 39]. Similarly, Malinski et al. [40] reported that this redox couple was not observed after demetalation of the film in acidic medium. The possible mechanism proposed by them was intermolecular electron transfer from the Ni(II) to the porphyrin ring after the two electron oxidation of the porphyrin ring to the dication. In aqueous media, the oxidation of dissolved Ni(II) to Ni(III) has been known to be very difficult due to the strong hydration of nickel ions. However, this effect does not exist when nickel is coordinated with highly hydrophobic polymeric film. The poly(Ni(4-TMPyP)) film were also synthesized on platinum, gold, and indium tin oxide electrodes in basic aqueous solutions.

The electrochemical properties of the poly(Ni(4-TMPyP)) films were evaluated after transferring them to a Ni(4-TMPyP)-free aqueous solution with pH 10 by cyclic voltammetric technique. Figure 1b shows that the poly(Ni(4-TMPyP))-modified electrode exhibited one electrochemically reversible redox couple with formal potential of $E^{\circ'} = 0.75$ V in an aqueous pH 10 that was performed at different scan rates. The inset of Fig. 1b shows plots of I_{pa} and I_{pc} vs scan rate. This behavior demonstrates about a

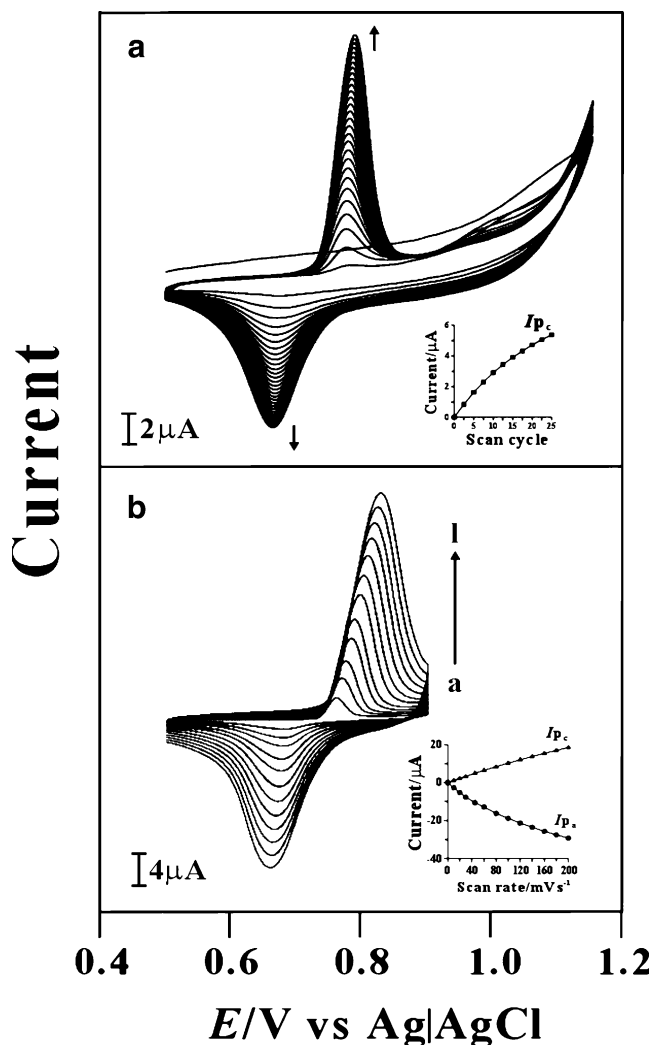


Fig. 1 **a** Repetitive cyclic voltammograms of 1×10^{-4} M Ni(4-TMPyP) in a pH 10 buffer aqueous solution. Scan rate: 0.1 V/s. Electrode: glassy carbon. The inset shows a plot of the cathodic peak current (I_{pc}) vs scan cycle. **b** Cyclic voltammograms of a poly(Ni(4-TMPyP)) film-modified glassy carbon electrode in a pH 10 aqueous solutions for scan rates of *a* 0.01, *b* 0.02, *c* 0.03, *d* 0.045, *e* 0.06, *f* 0.08, *g* 0.1, *h* 0.12, *i* 0.14, *j* 0.16, *k* 0.18, and *l* 0.2 V/s. The inset shows a plot of the peak currents I_{pc} and I_{pa} vs scan rates

near linear dependence of I_{pa} and I_{pc} on the scan rates. This behavior was found consistent with the surface-type behavior of a reversible, electron transfer process of a thin-layer film.

The peak current and scan rate are related as

$$I_p = n^2 F^2 v A \Gamma_0 / 4RT \quad (1)$$

where, Γ_0 , v , A , and I_p represent the surface coverage concentration, the scan rate, the electrode area, and the peak current, respectively. The above result indicated that the redox process was confined to the surface of the poly(Ni(4-TMPyP))/GC electrode, confirming the immobilized state of the poly(Ni(4-TMPyP)) [41, 42].

Electrochemical quartz crystal microbalance measurements and the electrochemical deposition process of poly(Ni(4-TMPyP)) in basic aqueous solutions

The cyclic voltammograms of the polymerization process of Ni(4-TMPyP) in pH 10 aqueous solution showed obvious one redox couple in the scanning potential region. The EQCM measurements and cyclic voltammetry were used to study in situ growth of poly(Ni(4-TMPyP)) film in the pH 10 aqueous solutions. Figure 2a demonstrates the consecutive cyclic voltammetry of Ni(4-TMPyP) on a gold electrode in an aqueous pH 10 solution. The electrodeposition process involved with an electrochemical oxidation

of monomer at more positive potential than 0.85 V (vs Ag|AgCl).

Figure 2b shows the change in the EQCM frequency recorded during the first ten cycles of the consecutive cyclic voltammetry. The increase in the voltammetric peak current in Fig. 2a and the frequency decrease (or mass increase) in Fig. 2b are consistent with the growth of a poly(Ni(4-TMPyP)) film on the gold electrode in basic aqueous solution. The results showed that the deposition occurred between the potentials of 0.85 and 1.1 V (vs Ag|AgCl). This behavior once again confirmed the anodic oxidation of porphyrinic ring which was followed by deposition of film on Au surface. In the EQCM experiments, the mass change at the gold electrode can be calculated from the change in frequency (assuming that the film to be a rigid resonator), as given in the Sauerbrey equation [43, 44]:

$$\text{Mass change } (\Delta m) = \left(-1/2\right)(f_o^{-2})(\Delta f)A(k\rho)^{1/2} \quad (2)$$

where, Δf is the observed frequency change, A is the area of the gold disk coated onto the quartz crystal, ρ is the density of the crystal, k is the shear modulus of the crystal, and f_o is the oscillation frequency of the crystal. A 1-Hz frequency change is equivalent to a 1.4-ng change in mass. During the first cyclic voltammetry scan, about 100 ng/cm² of poly(Ni(4-TMPyP)) film was deposited on the gold electrode and a total of about 742 ng/cm² of poly(Ni(4-TMPyP)) film was deposited on the gold electrode after the ten cyclic voltammetric scans. From the EQCM results, it was evident that a total amount of about 740 ng/cm² of poly(Ni(4-TMPyP)) was observed on the gold electrode after the first ten cyclic voltammetric scans, respectively.

The results also show that a poly(Ni(4-TMPyP)) film grew steadily vs time on a gold electrode. The EQCM measurements showed that the deposition of the film initiated at a starting potential of about 0.85 V, and then the main deposition occurred between the potentials of 0.85 and 1.1 V (vs Ag|AgCl) in aqueous solution of pH 10.

The effect of pH on electrochemical properties of poly(Ni(4-TMPyP)) films

Figure 3 shows the cyclic voltammograms of a poly(Ni(4-TMPyP)) film synthesized from a basic aqueous solution on a glassy carbon electrode that was then transferred to buffer aqueous solutions with pH (a) 8, (b) 9, (c) 10, (d) 11, (e) 12, and (f) 13. As the pH decreased, the anodic and cathodic peak currents and charge under the peaks decreased. However, the charges under cathodic and anodic peaks were found to be equal entire range of pH studied. Similarly, the peak separation between anodic and cathodic peak was also increased with the decrease of pH. The peak separation at pH 8 was 130 mV, whereas at pH 13 was 40

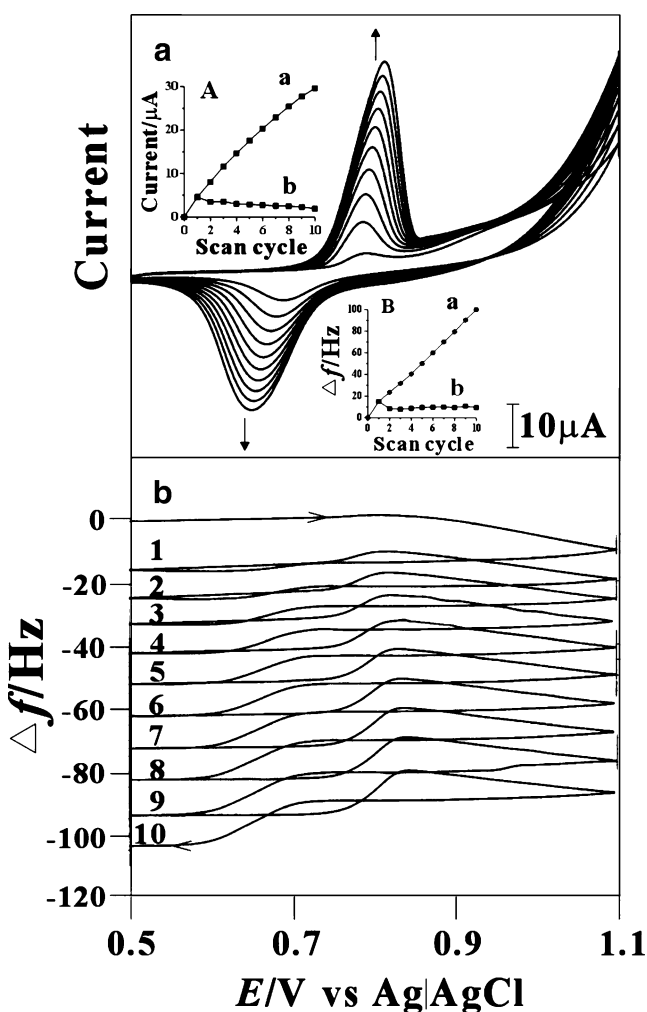


Fig. 2 a Consecutive cyclic voltammograms of poly(Ni(4-TMPyP)) synthesized from 1×10^{-4} M Ni(4-TMPyP) in a pH 10 buffer aqueous solution. Electrode: gold. Scan rate: 0.02 V/s. *Inset A* Plot of: a the total cathodic peak current (I_{p_c}) vs scan cycle and b the every cathodic peak current (I_{p_e}) vs scan cycle. *Inset B* Plot of: a the total frequency change Δf vs scan cycle and b the cycle frequency change of every cycle Δf vs scan cycle. b Change in EQCM frequency recorded concurrent with the first ten consecutive cyclic voltammogram cycles between potentials of 0.5 and 1.1 V

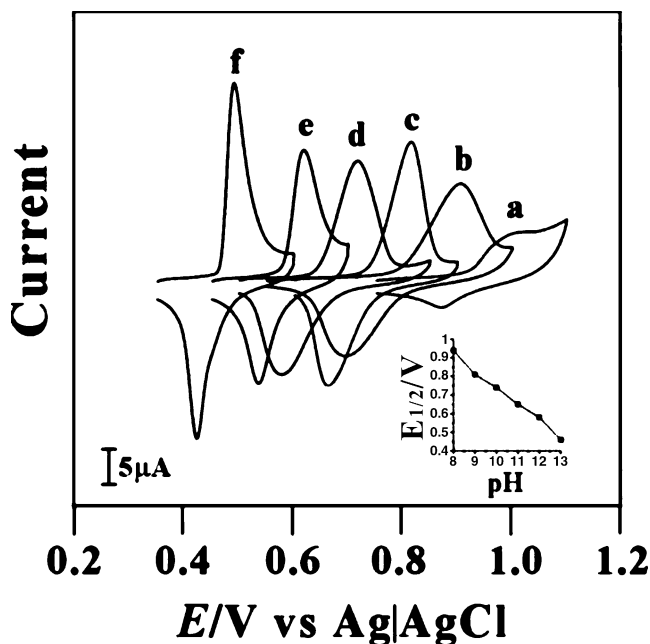
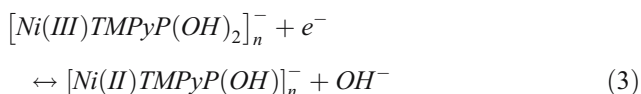


Fig. 3 Cyclic voltammograms of poly(Ni(4-TMPyP)) film-modified glassy carbon electrode in different buffer solutions with different pHs: *a* pH 8 (Tris), *b* pH 9 (Na₂B₄O₇), *c* pH 10 (NaHCO₃ + Na₂CO₃), *d* pH 11 (Na₂CO₃), *e* pH 12 (Na₂CO₃ + NaOH), and *f* pH 13 (NaOH)

mV. From the above results, it is understood that the species diffusing is the OH⁻ that maintains the charge balance. As would be expected, at lower pH, the increase in peak separation, peak cathodic broadening decreased peak currents observed indicate that the mass/charge transfer process in the cathodic process are slower and more affected by pH decrease. This behavior is due to lower availability of OH⁻. The cyclic voltammograms showed a redox couple, and that the value of ΔE_p, (E_{pc}–E_{pa}) was nonzero. The formal potential of the poly (Ni(4-TMPyP)) film plotted vs the pH was shown in Fig. 3 over range of pH 8–13. This plot shows a negative slope of 75 mV per pH unit change. Similar behavior was observed at other Ni-complex-modified electrodes [40, 45, 46]. Hence, the electrochemical reactions involved is given as scheme



Electrocatalytic oxidation of H₂O and H₂O₂ by poly (Ni(4-TMPyP)) film and biocatalyst system

The oxidation of water into oxygen was determined using poly(Ni(4-TMPyP)) film by cyclic voltammetry by applying different working electrode potential ranges in various pH aqueous solutions in the deoxygenated condition. The results showed of a new cathodic wave found between

–0.2 and –0.6 V, depending on the positive potential limit in various pH aqueous solutions (Fig. 4). The peak current of the new cathodic wave was found to increase with the increasing positive potential limit. The results showed that O₂ evolved during electrocatalytic oxidation of water was got reduced on reverse scan. The increase of pH values of electrolyte favored the O₂ evolution reaction.

The electrocatalytic oxidation of H₂O by poly(Ni(4-TMPyP)) film using the rotating ring-disk electrode method in a basic aqueous solution in the absence of oxygen was performed. (Figure not shown) The electrochemical oxidation of H₂O by a poly(Ni(4-TMPyP)) film-modified glassy carbon disk electrode and electrochemical reduction of O₂ by a bare glassy carbon ring electrode using the rotating ring-disk electrode method in a pH range of 9, 11.5, and 13.1 buffered aqueous solution. The result disclosed employing a poly(Ni(4-TMPyP)) film-modified glassy carbon disc electrode had led to appearance of an anodic peak current when potential was applied more positive than +0.65 V (vs Ag|AgCl), whereas a cathodic peak current was obtained at the bare glassy carbon ring electrode. When the anodic peak current of the poly(Ni(4-TMPyP)) film-modified glassy carbon disc electrode increased, the cathodic peak current of the ring electrode increased, too.

The anodic current due to the H₂O oxidation has been shown in following equations:



While for the cathodic current, are the following equations:



The collection efficiency, $N=I_R/I_D$, was about 0.2 for the electrocatalytic oxidation of H₂O by poly(Ni(4-TMPyP)) film. However, comparing this RRDE results to the reversible electrochemical reactions of the [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] redox couple showed a reversible oxidation current that occurred while using the bare glassy carbon ring electrode. The result of a plot of I_R/I_D vs ω showed a near-constant slope of 0.31 for the [Fe(CN)₆³⁻]/[Fe(CN)₆⁴⁻] redox couple (E_R=0.5 V) whereas the result of I_R/I_D was about 0.2 for the electrocatalytic oxidation of O₂ by Ni(4-TMPyP) film. These results are consistent about 65% of H₂O oxidized to O₂ and about 35% of H₂O oxidized to H₂O₂ by Ni(4-TMPyP) film with I_R being the oxidation current shown in Eq. 4 during the electrocatalytic oxidation of H₂O.

These results indicate that increase of pH and potential of the oxygen reduction towards positive side favored the hydrolysis of water into oxygen. The phenomenon may be due to the existence of higher oxidation state Ni ions in poly(Ni(4-TMPyP)) film. Malinski et al. [40] reported that based on X-ray photoelectron spectroscopy results, at higher positive potential amount of Ni(III) decreased which

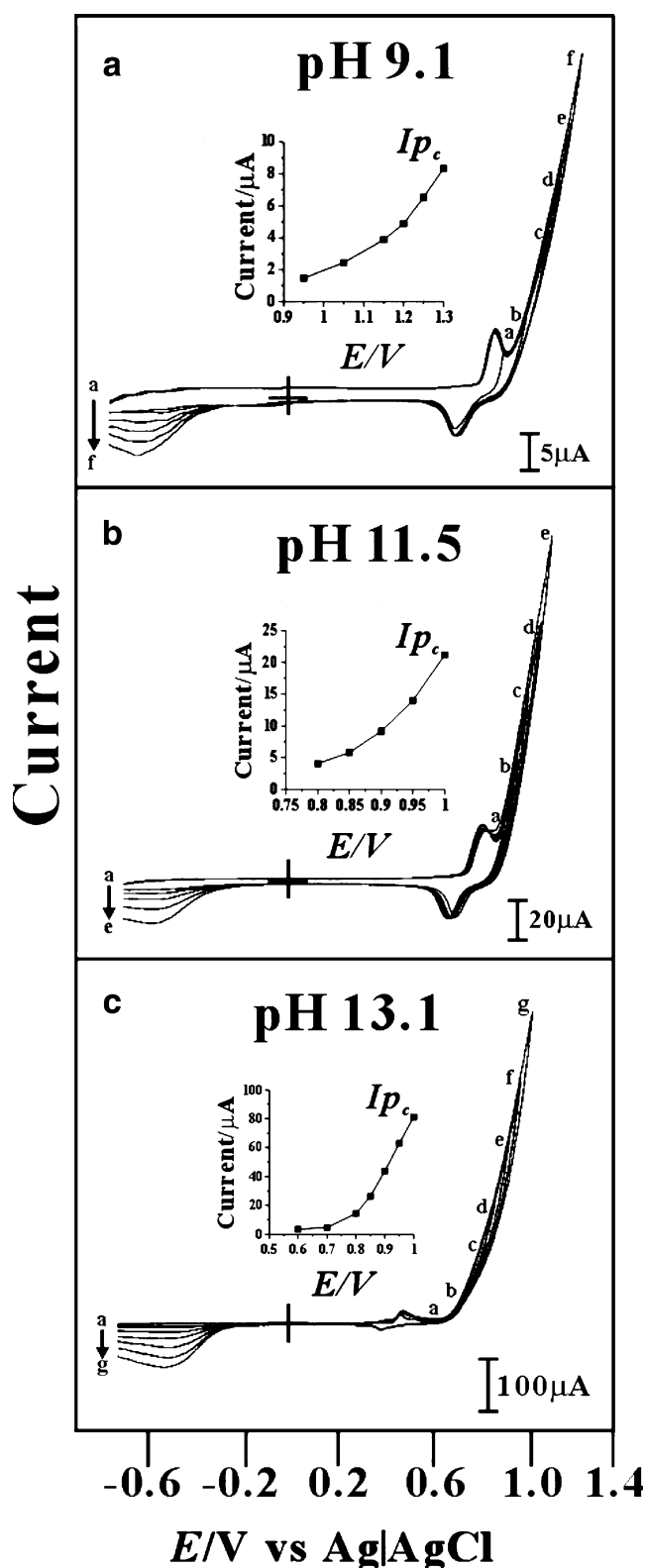
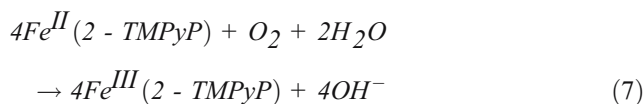
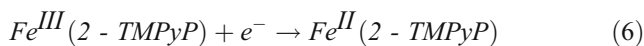


Fig. 4 a Effect of switching potentials of on oxidation of H₂O and on O₂ reduction at poly(Ni(4-TMPyP)) film in Na₂B₄O₇ buffer solution with pH 9.1 between -0.8 V and a 0.95, b 1.05, c 1.15, d 1.2, e 1.25, and f 1.3 V. Inset shows I_{p_c} of O₂ vs switching potentials of Ni(4-TMPyP) film. b Effect of switching potentials of on oxidation of H₂O and on O₂ reduction at poly(Ni(4-TMPyP)) film in pH 11.5 of Na₂CO₃ buffer solution between -0.75 V and a 0.8, b 0.85, c 0.9, d 0.95, and e 1.0 V. Inset shows I_{p_c} of O₂ vs switching potentials of poly(Ni(4-TMPyP)) film. c Effect of switching potentials of on oxidation of H₂O and on O₂ reduction at poly(Ni(4-TMPyP)) film in a pH 13.1 of NaOH buffer solution between -0.7 V and a 0.6, b 0.7, c 0.8, d 0.85, e 0.9, f 0.95, and g 1.0 V. Inset shows I_{p_c} of O₂ vs switching potentials of Ni(4-TMPyP) film

avored in their higher oxidation state. Hence, the catalysis of water at higher positive potential must be due to Ni(IV) or Ni(V) species.

Oxidation of water in to oxygen evolution by poly (Ni(4-TMPyP)) films were determined by a bicatalyst system at poly((Ni(4-TMPyP)) film in the presence of Fe(2-TMPyP) (iron tetrakis(*N*-methyl-2-pyridyl)porphyrin) in aqueous solution with pH 13 (Fig 5a). In the first segment, the scanning was started from 0.0 V and scanned towards to negative potential up to -1.0 V. However, the second and third segments were scanned between 1.0 and -1.0 V. In the first segment, the reduction peaks attributed to Fe(II) to Fe(I) and porphyrin ring were observed. Whereas, in the second segment, besides the oxidation peaks attributed to Fe(I) and porphyrin ring, the oxidation of Ni(II) to Ni(III) with oxygen evolution were obtained. Hence, in the third segment, a peak corresponds to oxygen reduction appeared at approximately -0.36 V in the presence of Fe(2-TMPyP). These results indicate that overpotential of oxygen reduction is relatively low and changes significantly in the presence of Fe(2-TMPyP). That is, overpotential has been reduced 200 mV when compared with condition in the absence of Fe(2-TMPyP). Figure 5b shows the cyclic voltammogram of above reaction in the same experimental conditions at GC in pH 13 aqueous solution. No oxygen reduction peak was observed at nonmodified electrode. This phenomenon shows that water has not been hydrolyzed at GC in this potential range. The reactions involved in the presence of Fe(2-TMPyP) are given as follows:



may be due to the existence of generation of higher valent species (Ni(IV) or Ni(V)) at oxygen evolution potential. Moreover, the oxygen attachment with nickel ions has been

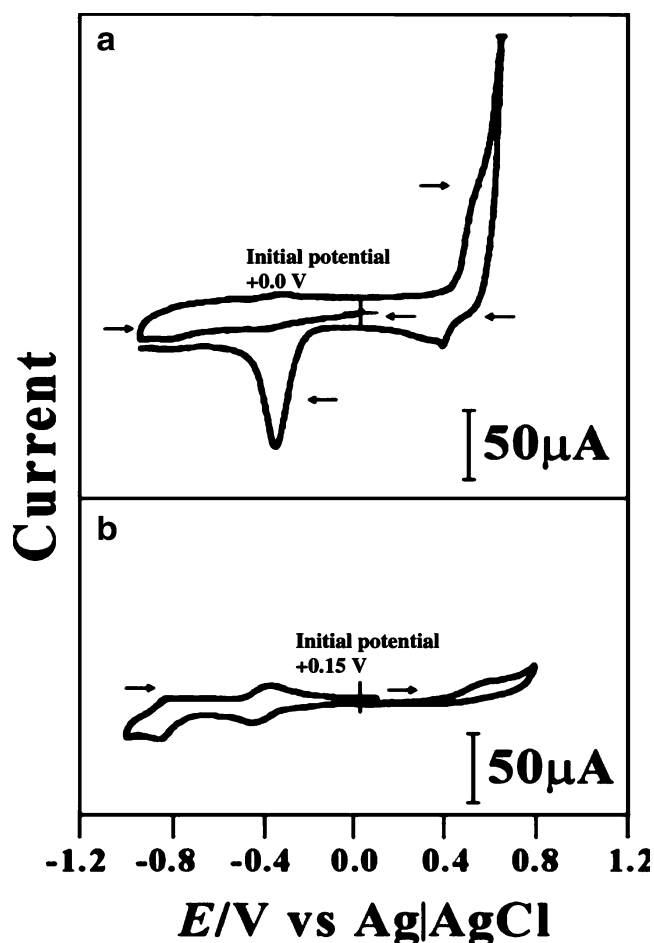


Fig. 5 **a** Cyclic voltammograms of poly(Ni(4-TMPyP))/GC electrode in pH 13.0 buffered solutions with Fe(2-TMPyP) in the absence of oxygen. **b** Cyclic voltammograms of bare GC in pH 13.0 buffered solutions with Fe(2-TMPyP) in the absence of oxygen. Scan rate 0.1 V/s

Electrocatalytic oxidation of H₂O₂

The electrocatalytic oxidation of H₂O₂ by poly(Ni(4-TMPyP)) film were determined by cyclic voltammetry in alkaline pH aqueous solutions (Fig. 6a). It also shows the CVs of poly(Ni(4-TMPyP)) film in the alkaline solution in the absence and presence of H₂O₂. The anodic peak current of the Ni(II) to Ni(III) oxidation peak of poly(Ni(4-TMPyP)) film at potential of about 0.43 V increased noticeably, while the cathodic peak current decreased as the concentration of H₂O₂ increased. However, on bare glassy carbon electrode, no H₂O₂ oxidation voltammetric signal was observed up to 0.7 V. This behavior indicates that H₂O₂ was oxidized into oxygen by mediated action of poly(Ni(4-TMPyP)) film. The H₂O₂ oxidation current responses showed a linear relationship with the concentration of H₂O₂ over the range of 0.025 to 0.1 M. Meanwhile, in the reverse cycle, the evolved oxygen during previous scan was reduced by poly(Ni(4-TMPyP)) film at a potential

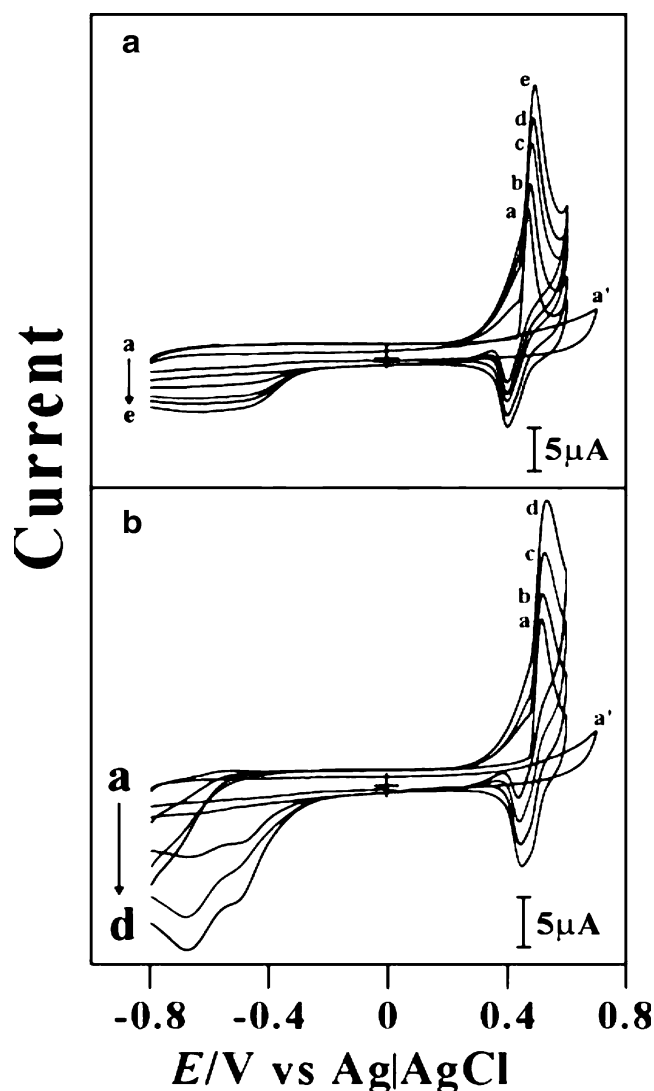
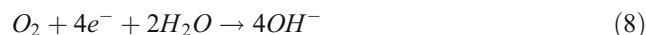


Fig. 6 Cyclic voltammograms of **a** at poly(Ni(4-TMPyP)) film in an aqueous solution with pH 13.1 and different concentrations of [H₂O₂]: **a** 0.0, **b** 2.5×10^{-2} , **c** 5.0×10^{-2} , **d** 7.5×10^{-2} , and **e** 1×10^{-1} M. **a'** Bare glassy carbon electrode and [H₂O₂]= 1×10^{-1} M; **b** poly(Ni(4-TMPyP))/GC film in pH 13.1 aqueous solution with hemoglobin and [H₂O₂]: **a** 0.0, **b** 2.5×10^{-2} , **c** 5.0×10^{-2} , and **d** 7.5×10^{-2} M. **a'** Bare glassy carbon electrode and [H₂O₂]= 7.5×10^{-2} M

above -0.4 V. Equation 8 shows reduction of oxygen at poly(Ni(4-TMPyP)) film.



The above-mentioned experiment was repeated in the presence of hemoglobin–Fe(II) catalyst (Fig. 6b). The results demonstrates that anodic peak current of the Ni(II) to Ni(III) oxidation peak of poly(Ni(4-TMPyP)) film at potential of about 0.43 V increased noticeably, while the cathodic peak current decreased as the concentration of H₂O₂ increased. However, addition of hemoglobin–Fe(II)

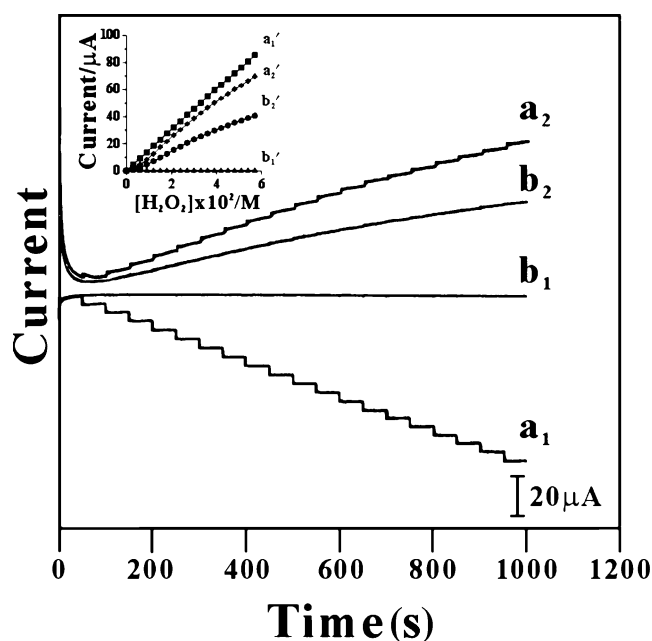


Fig. 7 Amperometric responses of 19 sequential additions of H_2O_2 (each 3×10^{-3} M) at a_1 poly(Ni(4-TMPyP)) film-modified disk (potential kept at +0.55 V in solution with pH 13.1), b_1 bare disk glassy carbon, a_2 poly(Ni(4-TMPyP)) film-modified ring (keep potential at -0.8 V), b_2 bare ring glassy carbon. Inset Plot of variation of catalytic current vs $[\text{H}_2\text{O}_2]$ at a_1' at poly(Ni(4-TMPyP)) film-modified disk b_1' bare disk glassy carbon, a_2' at poly(Ni(4-TMPyP)) film-modified ring b_2' at bare ring glassy carbon

catalyst relatively enhanced the oxygen reduction current at above -0.4 V by three times higher than that of its absence at poly(Ni(4-TMPyP)) film. This behavior depicts that hemoglobin-Fe(II) catalyzed the reduction of oxygen through mediated action and thereby the hemoglobin-Fe(II) was oxidized back to hemoglobin-Fe(III).

Stability of poly(Ni(4-TMPyP)) film-modified disk for H_2O_2 measurement

Figure 7a,b shows the response obtained for 19 successive addition of 3×10^{-3} M concentration of the H_2O_2 solution in aqueous solution with pH 13.1 at poly(Ni(4-TMPyP)) film-modified disk glassy carbon electrode and bare GC, respectively, at 0.55 V. No significant decrease in the catalytic current was observed up to 19 additions for oxidation of H_2O_2 . However, at bare GC surface, no catalytic current of oxygen evolution was observed up to 19 additions at 0.55 V. Figure 7a,b shows the electrocatalytic reductive reaction of oxygen evolved at ring electrode in the above condition at poly(Ni(4-TMPyP)) film-modified disk and bare GC, respectively, at 0.8 V. The sensitivity of oxygen reduction at poly(Ni(4-TMPyP)) film-modified ring electrode was found nearly two times higher than that of the bare GC ring electrode. These results also

indicated that the operational stability of the electrode was good up to 0.057 M concentration of H_2O_2 .

Electrocatalytic oxidation of adenine and guanine by film-modified electrodes

The electrocatalytic oxidation of adenine and guanine by Ni(4-TMPyP)-modified film was also performed in pH 10 aqueous solution.

Figure 8a shows the cyclic voltammograms of a poly(Ni(4-TMPyP))-modified electrode in pH 10 aqueous solution with various concentrations of adenine. Figure 8b shows the cyclic voltammograms of a poly(Ni(4-TMPyP))-modified electrode in pH 10 aqueous solution with various concentrations of guanine. The redox couple of the film was at $E^{\circ'} = 0.75$ V. The anodic peak current of the redox couple increased noticeably, while its cathodic peak current decreased as adenine was increased. In the case of guanine, a broad peak was observed before oxidation commenced. This may be due to adsorption of guanine on GC surface. The result also showed increase in an anodic current due to oxidation of guanine by poly(Ni(4-TMPyP)) film (Fig. 8b). The experimental results indicated that the electrocatalytic oxidation of adenine by poly(Ni(4-TMPyP))-modified film was active. However, the experimental results showed that the electrocatalytic oxidation of guanine by Ni(4-TMPyP)-modified film was less active than adenine oxidation.

Figure 8c shows the electrocatalytic and electrochemical oxidations of adenine and guanine with various concentrations by poly(Ni(4-TMPyP))-modified film performed in pH 10 aqueous solution. The two anodic peaks were obtained at 0.65 and 1.03 V for oxidation of guanine and adenine, respectively. The peak oxidation currents were found to increase as the concentrations of adenine and guanine increased. Both the results indicated that the electrocatalytic oxidation of adenine by poly(Ni(4-TMPyP))-modified film remained active.

Electrocatalytic oxidation of N_2H_4 , NH_2OH , and L-cysteine by film-modified electrodes

The electrocatalytic oxidation of N_2H_4 , NH_2OH , and L-cysteine by poly(Ni(4-TMPyP))-modified film was also performed in pH 13.1 aqueous solution. Figure 9a showed the cyclic voltammograms of a poly(Ni(4-TMPyP))-modified electrode in pH 13.1 aqueous solution with various concentrations of N_2H_4 . Figure 9b showed the cyclic voltammograms of a poly(Ni(4-TMPyP))-modified electrode in pH 13 aqueous solution with various concentrations of NH_2OH . The anodic peak current of the redox couple of the film at $E^{\circ'} = 0.75$ V, was found to increase noticeably, while its cathodic peak currents decreased due

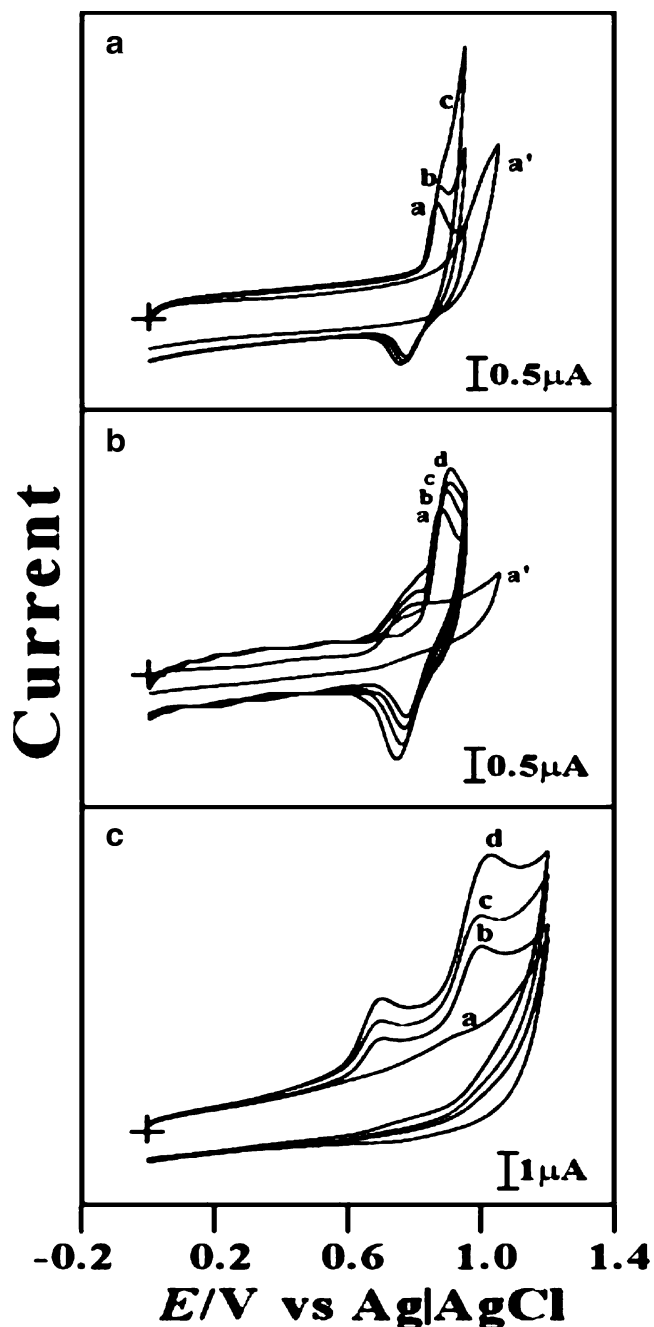


Fig. 8 Cyclic voltammograms of: **a** in aqueous solution with pH 10 and [adenine]: *a* 0.0, *b* 4×10^{-4} , and *c* 8×10^{-4} M. *a'* Bare glassy electrode and [adenine] = 8×10^{-4} M. **b** poly(Ni(4-TMPyP)) film aqueous solution with pH 10 and [guanine]: *a* 0.0, *b* 5×10^{-3} , *c* 1×10^{-2} , and *d* 1.5×10^{-2} M. *a'* Bare glassy electrode and [guanine] = 1.5×10^{-2} M. **c** Poly(Ni(4-TMPyP)) film in an aqueous solution of various concentrations of adenine and guanine with pH 10 and [adenine]: *a* 0.0, *b* 4×10^{-4} , *c* 8×10^{-4} M, and *d* 1.2×10^{-3} M; [guanine]: *a* 0.0, *b* 5×10^{-3} , *c* 1×10^{-2} , and *d* 1.5×10^{-2} M

to oxidation of N_2H_4 and NH_2OH by the Ni(4-TMPyP)-modified film (Fig. 9a,b). The experimental results indicated that the electrocatalytic oxidation of N_2H_4 and NH_2OH by poly-Ni(4-TMPyP)-modified film remained active.

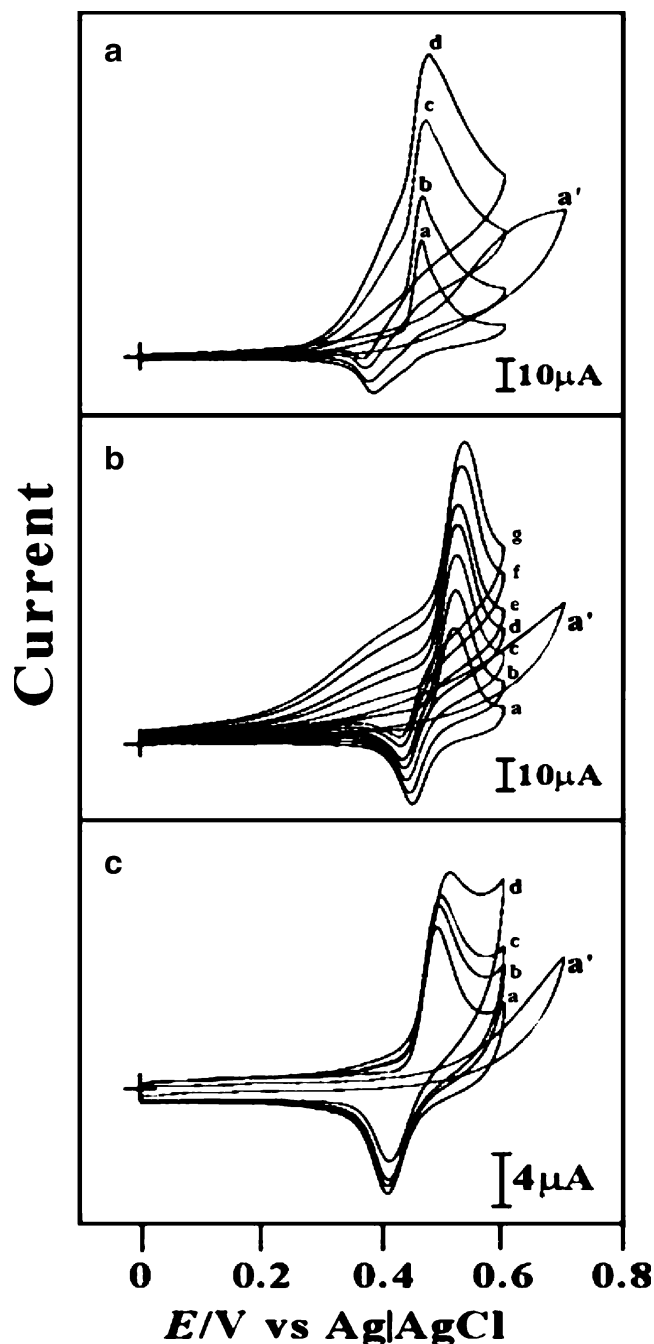


Fig. 9 Cyclic voltammograms of poly(Ni(4-TMPyP)) film in an aqueous solution with pH 13.1 and **a** [N_2H_4]: *a* 0.0, *b* 2.5×10^{-3} , *c* 5×10^{-3} , and *d* 7.5×10^{-3} M. *a'* Bare glassy electrode and [N_2H_4] = 7.5×10^{-3} M. **b** [NH_2OH]: *a* 0.0, *b* 1×10^{-4} , *c* 2×10^{-4} , *d* 3×10^{-4} , *e* 4×10^{-4} , *f* 5×10^{-4} , and *g* 6×10^{-4} M. *a'* Bare glassy electrode and [NH_2OH] = 6×10^{-4} M. **c** [L-cysteine]: *a* 0.0, *b* 7×10^{-3} , *c* 1.4×10^{-2} , and *d* 2.1×10^{-3} M. *a'* Bare glassy electrode and [L-cysteine] = 2.1×10^{-3} M

Figure 9c shows the electrocatalytic oxidation of L-cysteine by Ni(4-TMPyP)-modified film performed in the pH 13 aqueous solution. The anodic peak current of the redox couple of the film at $E^{o'} = 0.75$ V, was found to increase noticeably, while its cathodic peak currents

decreased due to oxidation of L-cysteine by the Ni(4-TMPyP)-modified film (Fig. 9c).

The anodic peak current of the redox couple increased noticeably, while its cathodic peak current decreased due to the increase in the concentration of L-cysteine. The results indicated that the electrocatalytic oxidation of L-cysteine by Ni(4-TMPyP)-modified film was active.

Amperometric application in catalytic oxidation of N_2H_4

A typical amperometric, $i-t$, experiment of N_2H_4 was performed in a well-stirred solution (rotation speed 1,500) by keeping the disc electrode potential at +0.55 V in pH 13 aqueous solution. In the amperometric experiment, a good response was obtained for the 19 sequential additions of each 3×10^{-3} M N_2H_4 on the poly(Ni(4-TMPyP))/GC-modified disc electrode (Fig. 10). It was observed that the oxidation current of N_2H_4 increased with the addition of N_2H_4 (the disc electrode) and reached the steady state within a short time. The disc electrode current responses showed a linear relationship with the concentration of N_2H_4 over the range of 0–0.12 mM. The electrocatalysis of N_2H_4 on the bare GC disc electrode was carried out in the above-mentioned conditions and compared with the above results. The oxidation current of N_2H_4 on disc bare GC electrode both showed less current than the electrocatalysis of N_2H_4 on the poly(Ni(4-TMPyP))/GC-modified in the above-mentioned conditions. These results indicated that the poly(Ni(4-TMPyP))-modified electrode, hence could be used for good and accurate measurement of N_2H_4 .

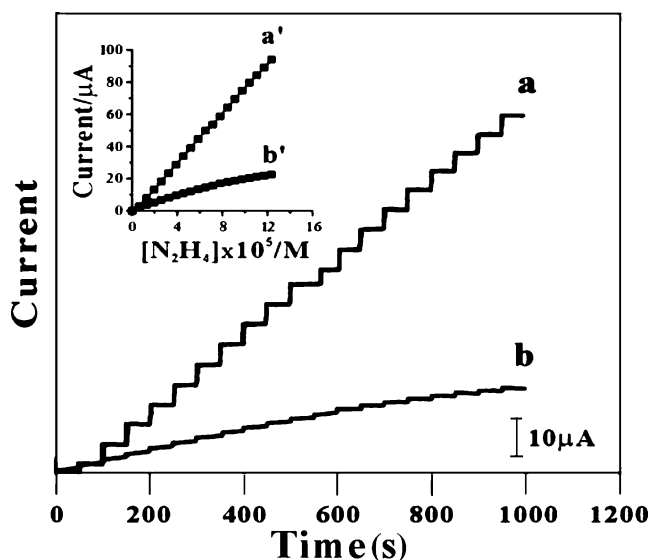


Fig. 10 Amperometric responses of 19 sequential additions of L-cysteine (each 6.5×10^{-6} M) at *a* disk-modified with poly(Ni(4-TMPyP)) film *b* bare disk glassy carbon. *Inset* Plot of variation of catalytic current vs [L-cysteine] at *a'* disk-modified with poly(Ni(4-TMPyP)) film and *b'* bare disk glassy carbon in pH 13 aqueous solution

Conclusions

By consecutive cyclic voltammetry, poly(Ni(4-TMPyP)) film-modified electrodes were synthesized on glassy carbon, platinum, gold, and ITO-modified electrodes from aqueous solution containing Ni(4-TMPyP) directly. Electrodeposition of nickel tetrakis(*N*-methyl-4-pyridyl)porphyrin (Ni(4-TMPyP)) produced stable and electrochemically active films in basic aqueous solutions. The electrochemical quartz crystal microbalance and cyclic voltammetry were used to study the in situ growth of poly(Ni(4-TMPyP)) immobilized films. The polymer films showed one redox couple and the formal potential was pH dependent when transferred to basic aqueous solutions.

This paper also discussed the electrocatalytic oxidation of H_2O , H_2O_2 , and reduction of the product (O_2) in a bicatalytic system. The two catalysts used were formed from Ni(4-TMPyP) film and Fe(2-TMPyP) in aqueous solution. The product of H_2O oxidation might have been enhanced by the electrocatalytic reduction of O_2 through the Fe(II)(2-TMPyP) [or hemoglobin-Fe(II)] species.

Cyclic voltammograms and the RRDE voltammograms of poly(Ni(4-TMPyP)) film-modified electrode in solution containing different concentrations of H_2O , H_2O_2 , adenine, NH_2OH , N_2H_4 , and L-cysteine showed active electrocatalytic oxidation behavior. A typical amperometric ($i-t$) experiment of H_2O_2 (and the product O_2) N_2H_4 was performed in a well-stirred solution (rotation speed 1,500) by keeping the electrode potential disc at +0.55 V and ring at -0.8 V for 19 sequential addition of H_2O_2 , N_2H_4 , respectively. The simultaneous determination of adenine and guanine was also performed at the poly(Ni(4-TMPyP)) film-modified electrode. The poly(Ni(4-TMPyP))-modified electrode resolved two well-defined peaks for adenine and guanine.

Acknowledgment This work was supported by the National Science Council of the Taiwan (ROC).

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