



Electrochemical fabrication of conducting polymer of Ni-porphyrin as nano-structured electrocatalyst for hydrazine oxidation



S.H. Kazemi^{a,b,*}, B. Hosseinzadeh^a, S. Zakavi^a

^a Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran

^b Center for Research in Climate Change and Global Warming (CRCC), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran

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ABSTRACT

Herein, we report a facile two electrochemical steps method for fabrication of conducting polymer of (5,10,15,20-tetra(4-sulfophenyl) porphyrin-nickel. Scanning electron microscopy was used to study the morphology of conducting metallopolymer nanoparticles. Also, electrochemical behaviors of conducting metallopolymer nanoparticles modified electrode were studied by cyclic voltammetry. It was found that the modified electrode demonstrates excellent electrocatalytic activity toward oxidation of hydrazine. Electro-oxidation of hydrazine was investigated using cyclic voltammetry and chronoamperometry techniques. The limit of detection and sensitivity of the modified electrode toward hydrazine were 0.11 μM and 1 mA mM^{-1} , respectively. Moreover, diffusion coefficient ($D = 4.19 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and catalytic rate constant ($k_{\text{cat}} = 44 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) at the metallopolymer modified electrode were determined using chronoamperometry.

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1. Introduction

Currently conducting polymers are important materials play important roles in a wide variety of applications including energy storage, microelectronics, electrochromic displays, electrocatalysis and chemical sensors [1–4]. An important class of conducting polymers is conducting metallopolymer, containing various metal centers from main groups or transition metals. The metal centers can be located either in the polymer main chain or in the side group structure [5,6]. Recently, modification of electrodes with conducting polymers, especially metallopolymer, has attracted enormous attentions [7–10]. Among the various procedures for modification of electrodes, electrochemical polymerization is an effective, controllable and facile strategy to prepare metallopolymer coated electrodes. Electrochemical modification usually proceeds by oxidation (or reduction) of an appropriate metal complex monomer to form a polymeric film [11–15]. Electrochemistry of nickel and nickel-based electrodes in the alkaline media is an important area for researchers. The electrode modified with thin film of polymers of nickel macrocycle (salen, porphyrins, phthalocyanines, etc.)

shows high catalytic activity toward electro-oxidation of organic compounds containing –OH and –NH₂ functional groups [16–19].

Hydrazine as an important example of –NH₂ containing compounds is a strong reducing agent widely used in industrial factories and agricultural applications [20,21]. Of note, hydrazine may cause some carcinogenic and hepatotoxic effects. It may cause liver and kidney damages, also irreversible deterioration of nervous system when it absorbs through skin [22–24]. Accordingly, determination of hydrazine in environmental and medical samples is of high importance. Thus, several methods have been employed for this purpose; including potentiometry, fluorimetry and spectrophotometry [23,25,26]. However, the overpotential of hydrazine electro-oxidation is usually high at conventional electrodes, thus a wide variety of modified electrodes have been developed to decrease this overpotential and enhance the electron transfer rate [27–33]. Among them, nanoparticle modified surfaces have attracted widespread interest in recent years due to the substantial enhancement in electron transfer rate and catalytic properties [34–36].

Recently, we have introduced a facile two steps electrochemical method for fabrication of nickel–curcumin conducting polymer in the form of segregated nanoparticles [6]. In the present article we report a continuation of the previous work devoted to the fabrication of the conducting metallopolymer nanoparticles. Herein, nanoparticles of conducting polymer of poly-(5,10,15,20-tetra(4-sulfophenyl) porphyrin-nickel) (Ni-TPPS₄) were electrodeposited on the glassy carbon electrode (GCE). The electrochemical

* Corresponding author at: Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran. Tel.: +98-2433153121; fax: +98-2433153232.

E-mail address: habibkazemi@iasbs.ac.ir (S.H. Kazemi).

behaviors of PNi-TPPS₄-NPs modified electrode were investigated using cyclic voltammetry (CV) and chronoamperometry. Also, field emission scanning electron microscopy (FESEM) was employed to study morphology of PNi-TPPS₄-NPs nanostructures. It should be considered that the fabrication of PNi-TPPS₄-NPs modified electrode is facile and small amount of starting materials required (especially the porphyrin monomer) to modify the electrode surface. The working electrolyte for modification of the electrode is aqueous solution, so there is no need to use organic solvents. Also, the modified electrode shows excellent stability and reproducibility after several successive cycles of electro-oxidation of hydrazine. The results confirm that the GCE modified with PNi-TPPS₄ nanoparticles provides high electrocatalytic activity toward oxidation of hydrazine.

2. Experimental

All reagents were of analytical reagent grade and used without further purification. Sodium hydroxide was obtained from Merck. Sodium dihydrogen phosphate, ammonium chloride, sodium chloride; nickel nitrate hexahydrate and hydrazine were purchased from Sigma–Aldrich Company.

5,10,15,20-tetraphenyl porphyrin (H₂TPP) and 5,10,15,20-tetra(4-sulfophenyl) porphyrin (H₂TPPS₄) were synthesized as described elsewhere [37–40]. All solutions were prepared using doubly distilled water and all experiments were performed at room temperature.

Electrochemical measurements were carried out using a potentiostat/galvanostat (PGSTAT101, Autolab, Eco Chemie, The Netherlands), in a conventional three electrode cell containing glassy carbon (GC, 1.8 mm diameter), a platinum wire and an Ag/AgCl (saturated KCl solution) as working, counter and reference electrodes, respectively. Prior to electrodeposition, the bare GCE was polished with 0.03 and 0.5 μm of alumina slurry to achieve a mirror-like surface, and subsequently sonicated in distilled water for 5 min. The polished GCE was immersed in a 0.1 M of phosphate buffer solution and the potential was scanned between 0 and +1.5 V vs. reference electrode at a scan rate of 100 mV s⁻¹ until a reproducible voltammogram was obtained.

Fabrication of PNi-TPPS₄-NPs was performed using a two steps electrochemical process. First, nickel nanoparticles (Ni-NPs) were electrodeposited on the GCE using a potential step of -0.8 V for 120 s in a 10 mM of nickel nitrate solution containing ammonium chloride (1 M) and sodium chloride (1 M). Then, modified electrode was immersed in 25 ml NaOH (0.1 M) containing 1 mg TPPS₄ and potential scanned between 0 and +1 V for at least 12 cycles at a scan rate of 100 mV s⁻¹. The pH of this solution was adjusted at 8.3. The pH adjustment is necessary for the first step to ensure formation of Ni-NPs. In the next step and during all electrochemical studies the electrolyte solution is NaOH (0.1 M).

3. Results and discussion

3.1. Ni-NPs and PNi-TPPS₄-NPs electrodeposition

In order to find the optimum potential for fabrication of Ni-NPs, cyclic voltammogram of GC electrode in nickel nitrate solution was recorded (Fig. 1); and four potentials were chosen accordingly. As shown in Fig. 1, the reduction of nickel ions and deposition of Ni-NPs take places at potentials more negative than -0.8 V. However, at potentials more negative than -1.3 V, it was seen that electrodeposition may be prevented because of the formation of large H₂ bubbles. Hence, the potential of -1.3 V was chosen as electrodeposition potential in potential step procedure. A plot of peak current against deposition time for Ni-NPs deposition on the GC electrode

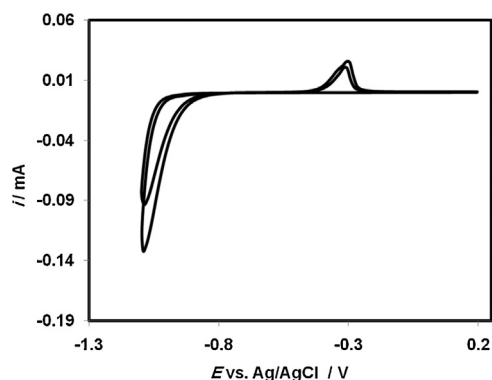


Fig. 1. Cyclic voltammograms of the GC electrode in Ni(NO₃)₂ solution at a scan rate of 100 mV s⁻¹.

in Ni(NO₃)₂ solution at a scan rate of 100 mV s⁻¹ is provided as supplementary information (Fig. S-1).

Ni-NPs modified GC electrode was subjected into NaOH solution containing H₂TPPS₄ monomer to form Ni-TPPS₄ conducting polymer nanoparticles. Electropolymerization was performed using consecutive cyclic voltammetry between 0 and +1 V at a scan rate of 20 mV s⁻¹ as shown in Fig. 2. As seen in Fig. 2, two redox processes were occurred. The first pair of redox peaks appeared in the range of +0.3 to +0.5 V vs. reference electrode can be attributed to the Ni(II)/Ni(III) oxidation reduction process which is a quasireversible process. The second wave may attributed to the polymer chain (porphyring ring) oxidation process. The peak currents increased during successive potential cycling, indicating the polymerization of Ni-TPPS₄ monomers (formed at Ni-NPs surface, FTIR spectra are provided as supplementary information, Fig. S-2). It should be noted that Ni(II) will be formed during the anodic potential scan at the surface of Ni-NPs, thus electropolymerization around this nanoparticles will occur. Fig. 3 illustrates SEM images of Ni-NPs and PNi-TPPS₄-NPs modified surfaces. As seen in Fig. 3, Ni-NPs were fabricated in the first electrochemical step as a regular dispersion at the surface of the electrode. The size of the nanoparticles becomes larger after electropolymerization, confirming polymerization around the surface of Ni-NPs (Fig. 3a and b).

3.2. Optimization of time for deposition of nickel nanoparticles

In order to optimize the amount of Ni-NPs on the electrode surface, various deposition times were utilized at -1.3 V in electrolyte

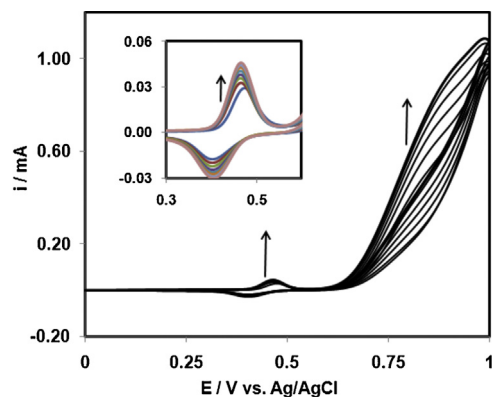


Fig. 2. Successive cyclic voltammograms recorded during electropolymerization of Ni-TPPS₄ on GC electrode in 0.1 M of NaOH containing TPPS₄ monomer at a scan rate of 20 mV s⁻¹. Inset shows the magnification of redox peaks between 0.3 and 0.5 V for better representation of the peak growth during polymerization.

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