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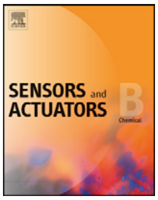

# High sensitivity amperometric and voltammetric determination of persulfate with neutral red/nickel oxide nanowires modified carbon paste electrodes

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ABSTRACT

A novel, highly sensitive sensor for detection of persulfate ($S_2O_8{}^{2-}$) is demonstrated by modification of carbon paste electrode (CPE) with nickel oxide nanowires (NiOx NWs) and neutral red (NR). Ni NWs are prepared by DC electrodeposition of Ni in the cylindrical pores of anodized aluminum oxide (AAO) templates. NWs are released, oxidized and immobilized with NR on the surface of CPE. Cyclic voltammetry studies demonstrate a pair of well-defined nearly reversible redox couples ($E^{\circ\prime} = -0.2$ V in a buffer solution pH 2.0) at a wide pH range of 1–12. The surface coverage and heterogeneous electron transfer rate constant of the adsorbed redox couple are $7.368 \times 10^{-12}$ mol cm$^{-2}$ and 7.9 s$^{-1}$, respectively, indicating a high NR loading efficiency for NiOx NWs and efficient electron transfer between redox couple and the electrode. The modified CPE exhibits an excellent electrocatalytic activity for a $S_2O_8{}^{2-}$ reduction, with a measured $k_{cat}$ of $\sim 7.14 \times 10^3$ M$^{-1}$ s$^{-1}$. This catalytic reduction allows an amperometric detection of $S_2O_8{}^{2-}$ at a potential of −0.2 V with detection limit of 30 nM, concentration calibration range of 0.1 μM to 12 mM and a linear sensitivity of 647.33 nA μM$^{-1}$, respectively.

## 1. Introduction

The phenazine dye, natural red (NR; N$^8$, N$^8$, 3-trimethylphenazine-2,8,-diamine chloride) (Scheme 1), has similar chemical structures as other planar dyes that belongs to the acridine, thiazine and xanthene groups [1,2]. NR has been utilized in various applications such as pH indicators in biochemical systems [3], optical sensors [4], DNA analysis [5,6], and virus detection [7]. Phenazine NR and other phenazine derivatives [8], particularly toluidine blue [9,10], meldola blue [11], Prussian blue [12–14], celestine blue [15,16], methylene blue [17], methylene green [18], azure A [19], azure B [20], thionine [21–23], and orthophenylendimines [24] have been considered as good candidates for artificial enzyme substrates and as redox mediator for electrochemical investigations of biological redox systems, in view of their low cost and efficient electron transfer. NR has been used as a redox mediator in the promotion of electrochemical enzyme biosensors [25–30], since it has a lower redox potential than phenothiazine and phenoxazines, due to having nitrogen as its second heteroatom instead of a divalent oxygen or sulfur [31]. Monomer or polymer derivatives of NR are also excellent redox mediators for enzyme biosensors (particularly in acidic and neutral media) in the potential range of −0.35 to −0.25 V [1].

In addition, NR shows excellent electrocatalytic activities [32,33], including a reversible voltammetric waves of NAD/NADH reduction/oxidation for NR modified electrodes [34] and electrocatalysis role in the reduction of $BrO_3{}^-$, $IO_3{}^-$, $O_2$, $NO_2{}^-$, $SO_5{}^{2-}$, $IO_4{}^-$, and $Cr_2O_7{}^{2-}$ for acidic aqueous solutions of NR polymer derivatives [1]. However, lack of long-term stability for dye-modified electrodes is a major deficiency [2,35]. Examples of remedies that have been explored for improving the stability and the electrochemical replication of phenazine derivatives include conventional immobilization mechanisms such as electropolymerization and physical adsorption [15]. In particular, electropolymerization of NR is facilitated by the presence of an amino functionality on its heteroaromatic phenazine ring [34].

In recent years, several nanostructures have been utilized for enhanced immobilization of phenazine dye on the electrode surfaces [15,16,36]. For instance, multi-walled carbon nanotubes (MWCNTs) are used for immobilization of NR [37] with improved loading and enhanced electrochemical activity in comparison to other carbon-based electrodes. Wang et al. [2] have reported

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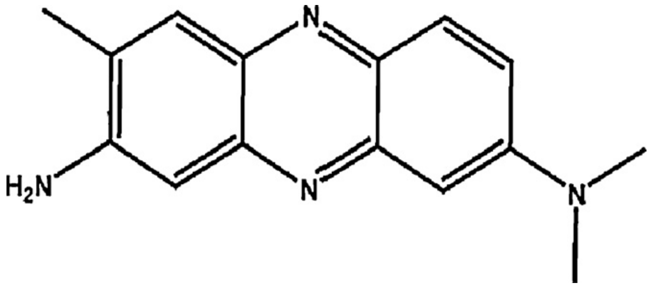
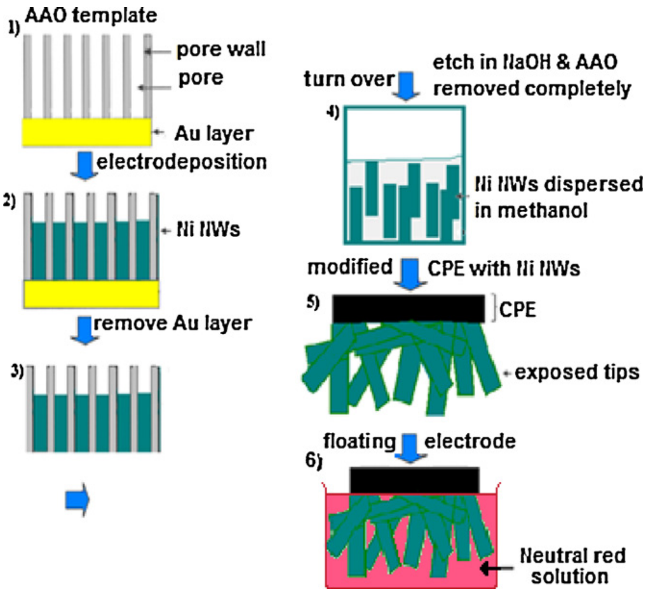


**Scheme 1.** Chemical structure of NR monomer.



**Scheme 2.** Schematic cross-section of steps of NR/NiOx NWs/CPE fabrication.

CNT/NR composite modified electrodes for electrocatalytic detection of Rutin. Moreover, sensors with MWCNT/NR modifications have been demonstrated for amperometric detection of hydrogen peroxide [38]. In comparison to CNTs, metallic NWs possess two advantages, namely, accurately controlled material characteristics through controlled synthesis process [39], and, the inherent presence of oxide layer on the surface of NWs, providing opportunities for various functionalization and blocking chemistries [40].

NWs have been fabricated using different methods such as chemical vapor deposition [41], electroless growth [42], and electrodeposition [43]. Among these, template-assisted electrodeposition method appear to be promising for metallic NWs due to the simplicity and the high level of control over the morphology, microstructural properties, packing density, size, and physical properties of the NWs by tuning the template and electrodeposition parameters. Polycarbonate films as well as anodized aluminum oxide (AAO) are the most popular templates that have been employed so far. AAO is preferred in comparison to polycarbonate templates due to its mechanical stability and its parallel and uniform high aspect ratio cylindrical pores. Direct current (DC) electrodeposition has been proved to be a useful technique for fabrication of Ni NWs as it provides a substantial control over the composition and the crystallinity of the NWs [44].

Persulfate is a strong oxidant and has been used for many applications such as water and soil decontaminants [45], circuit board fabrication [46], cosmetics [47], and polymerization [48]. It has been reported that persulfate may either cause or intensify diseases such as asthma [49] and skin reactions [50]. Because of a gradual increase in application of persulfate finding a simple and convenient measurement of persulfate is desired. Therefore, many studies have been performed in the recent years for the quantitative determination of persulfate [51,52].

This paper reports fabrication of presulfate sensors, where NR is physically immobilized on NiOx NWs CPE surface through a three-step (Scheme 2) modification method. The Ni NWs are electrodeposited in an AAO template (first step) and then obtained by dissolving the template using NaOH (second step). Finally, CPE surface is modified by NiOx NWs, followed by immobilization of NR. voltammetric and amperometric behavior of the NR immobilized NiOx NWs electrodes are systematically characterized and employed for detection of $S_2O_8^{2-}$.

## 2. Experimental

### 2.1. Chemicals and reagents

Anodized aluminum oxide (AAO, Whatman International Ltd.) membranes with average pore diameter of 100 nm and thickness of 60 μm were used as template for nanowire synthesis. The pore density and wall thickness of AAO templates were evaluated by scanning electron microscope (SEM, Vega-Tesacn) to be $\sim 8.0 \times 10^8$ cm$^{-2}$ and 100 nm, respectively. High purity graphite powder and NR (Merck) were used as received. Solutions were prepared from analytical reagent grade chemicals without further purification using double distilled water. The phosphate buffer (PB) solutions (0.1 M) were prepared from $H_3PO_4$, $NaH_2PO_4$ and $Na_2HPO_4$. The pH of PB solutions was adjusted with HCl and NaOH solutions. $NiCl_2$, $H_3BO_3$ and other reagents were of analytical grade. Pure $N_2$ (99.999%) was passed through the solution to avoid possible oxidation during the experiments.

### 2.2. Apparatus

Ni NWs were electrodeposited in a cylindrical Pyrex two-electrode homemade electrochemical cell. A 1 cm$^2$ Pt plate was used as anode electrode and an AAO template mounted on the other side of the cell as working electrode. The electrodes are placed parallel with a distance of 30 mm during the electrodeposition process. The electrodeposition current and voltage were measured by a Keithley 2001 multimeter. The experiments were performed with a computer controlled μ-Autolab modular electrochemical system (Eco ChemieUltecht), driven with GPES software (Eco Chemie). A conventional three-electrode cell was used with a Ag/AgCl/(sat KCl) reference electrode, a Pt wire as the counter electrode and NiOx NWs/CPEs as the working electrode. Voltammetry on CPE coated with NR/NiOx NWs were carried out in buffers free of NR molecules. The surface morphology of modified electrodes was studied with a SEM.

### 2.3. Preparation of Ni NWs

Ni NWs were prepared using conventional electrodeposition method [44]. One side of the AAO template was first coated with a 400 nm gold film using a thermal evaporator system to block one end of the pores and serve as cathode. Ni NWs are DC electrodeposited in AAO templates with current density of 0.8 mA/cm$^2$ using a Pt plate as an anode electrode and solution contains $NiCl_2$ (0.3 M) and 45 g/dm$^3$ of $H_3BO_3$ as electrolyte. The bath temperature and pH were maintained constant at 25 °C and 4.0, respectively. In order to release the Ni NWs from the AAO template, the Au film was mechanically polished and template was immersed in the 0.05 M NaOH solution to remove the AAO template and oxidize the NWs. NiOx NWs were then washed several time with double distilled water and finally dispersed in methanol.