

Nile Blue-hexacyanoferrate carbon paste modified electrode as an amperometric sensor for determination of hydrazine

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The main problem associated with metal hexacyanoferrates (MHCFs) is their instability at high pH values. We synthesized a new Prussian Blue analogue, Nile-Blue hexacyanoferrate (NBHCF), that remains stable in 0.2 M KOH. A carbon paste (CPE) chemically modified electrode (ME) containing NBHCF was prepared as a stable electrochemical sensor for measuring hydrazine. A detailed characterization of the electrochemical and electrocatalytic behavior of NBHCF was performed using cyclic voltammetric, chronoamperometric, differential pulse voltammetric (DPV) and hydrodynamic amperometric methods. The NBHCF-modified electrode produced reproducible redox peaks and resulted in a linear increase in the oxidation signal of hydrazine with increasing concentration of hydrazine in the range of 0.1-6.0 mM (in hydrodynamic amperometry method (HDA)). The electrode detection limit was 40 μM and possessed a surface coverage of $\Gamma = 2.0 \times 10^{-8} \text{ mol cm}^{-2}$.

Key Words: Modified electrode, carbon paste electrode, hexacyanoferrate, amperometric determination of hydrazine, Nile-Blue hexacyanoferrate

Introduction

Among the various mediators that have been used for electrode modification, solid metal hexacyanoferrates have attracted the attention of electrochemists as excellent electron transfer mediators. Since the work by

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Neff et al.¹ describing deposition of Prussian Blue (PB) on solid electrodes, interest in PB-like compounds has increased considerably. Transition metal complexes with hexacyanoferrate (MHCF) have been considered by many electrochemists in recent years, as a mediator for modified electrode preparation. Complexes formed with hexacyanoferrate have been made using a wide variety of transition metals.^{2–33} In addition, complex formation with hexacyanoferrate using organic compounds such as Ketotifen Fumarate,³⁴ Nile Blue [this work], and polymer³⁵ have also been assessed for their capacity to serve as a mediator. The main problem involving metal hexacyanoferrates (MHCFs) is their instability at higher pH values, as most metal hexacyanoferrates reported to date are stable only in neutral pH environments.^{6,17}

Hydrazine is a small, di-functional, and reactive molecule with good reducing capabilities that can participate in diverse reactions resulting in numerous applications. Hydrazine in particular is widely used as a catalyst, emulsifier, corrosion inhibitor, antioxidant, reducing agent, and oxygen scavenger.³⁶ More specifically, hydrazine is used for water treatment, in agriculture, in pharmaceuticals as a chemical blowing agent, as an oxygen scavenger in boilers and hot-water heating systems to control corrosion, and in a wide variety of other applications.³⁷ Therefore, the electro-oxidation of hydrazine is a reaction of practical importance and the detection of trace amounts of hydrazine is very important in the field of environmental and biological analysis. The electro-oxidation of hydrazine by different electrodes and mediators has been reported such as by using carminic acid as a homogeneous mediator,³⁸ palladium nanoparticles supported on a carbon ionic liquid electrode,³⁹ and palladium nanoparticle on carbon nanofibers (Pd/CNFs).⁴⁰ A comparative study of the electrocatalytic activities of some metal hexacyanoferrates for the oxidation of hydrazine has also been reported.⁴¹

Nile-Blue (NB) is a member of the benzophenoxazine class of dyes (Figure 1), which has been found to localize selectively in animal tumors. Members of this class of dyes exhibit relatively low systemic toxicity and some retard tumor growth temporarily. This study proposes and examines a novel dye hexacyanoferrate microstructure represented by Nile Blue hexacyanoferrate (NBHCF). Here, we have assessed the electrochemical behavior of a carbon paste electrode (CPE) prepared using a dye, NBHCF, as a modifier in measuring hydrazine.

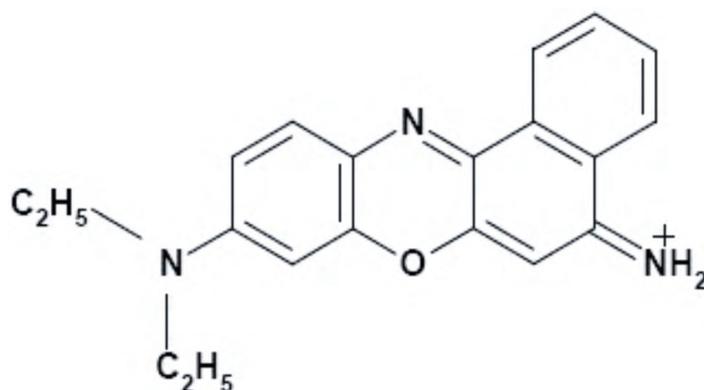


Figure 1. The structure of Nile-Blue (NB).

Experimental

Reagents and apparatus

NB and potassium hexacyanoferrate (II) were of analytical grade from Merck and used without any further purification. All other chemicals used in these investigations were of analytical grade. A solution of 0.2 M KOH was prepared to serve as a supporting electrolyte. The hydrazine solutions were prepared just prior to use. All solutions were prepared with double distilled water. Electrochemical experiments were carried out at 25 ± 1 °C using a potentiostat/galvanostat (BHP-2063 electrochemical analysis system, Behpajoo, Isfahan, Iran). A conventional 3-electrode cell was also used for electrochemical experiments. A saturated Calomel electrode, platinum wire, and NBHCF modified carbon paste electrode were used as reference, auxiliary, and working electrodes, respectively. Microstructure characterization of the NBHCF precipitate was performed using a Philips - XL30 low vacuum scanning electron microscope located in Tarbiat Modrres University, Tehran.

Preparation of the modified electrode

The NBHCF was prepared by using $K_4Fe(CN)_6$ and NB sulfate solutions. For the preparation of NBHCF, 50 mL of 0.1 M $K_4Fe(CN)_6$ was slowly added with agitation to 50 mL of 0.1 M NB sulfate solution. The NBHCF precipitate thus produced was then filtered, washed, and dried. The resulting precipitate was a blue powder that was stable in aqueous solution at pH settings well above 7. The CPE was prepared by homogenizing a mixture of graphite powder and NBHCF precipitate at a 5:1 ratio, respectively, along with 3 drops of paraffin. The resulting paste was then packed into a polyethylene tube. The electrode surface was renewed by extrusion of approximately 0.5 mm carbon paste from the holder and smoothed using filter paper.

Results and discussion

Voltammetric assessment of NBHCF-CPE

The cyclic voltammetric technique was used for studying the electrochemical properties of NBHCF-CPE. Typical cyclic voltammograms obtained with the NBHCF-CPE at different scan rates after immersing in a 0.2 M KOH solution are shown in Figure 2. Experiments using the NBHCF-CPE produced one pair of redox peaks associated with the 0.2 M KOH solution, having E_{pa} and E_{pc} potentials of 0.25 V and 0.12 V vs. SCE, respectively. The formal potential for this electrode, $E^\circ = (E_{pa} + E_{pc})/2$, was 0.18 V vs. that of the SCE. The peak-to-peak potential separation ($\Delta E_p = E_{pa} - E_{pc}$) in KOH solution was 0.13 V vs. SCE, for a potential sweep rate of 100 mV s^{-1} . The peak currents of the voltammogram are linearly proportional to the scan rate in the range $10\text{-}200 \text{ mV s}^{-1}$. For scan rates higher than 200 mV s^{-1} , the anodic and cathodic peak currents are proportional to the square root of the scan rate (not illustrated), which is expected for a diffusion-controlled electrode process. The relationship between the peak current and square root of scan rate for linear diffusion may be described as follows:

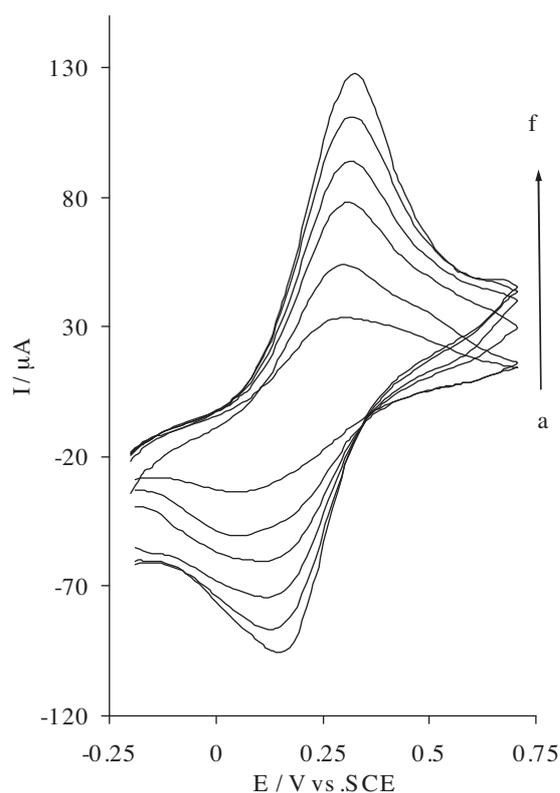


Figure 2. Cyclic voltammograms of NBHCF-CPE in 0.2 M KOH using different scan rates, (a-f: 50, 100, 200, 300, 400 mV s^{-1}).

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}Cv^{1/2}$$

where D is the diffusion coefficient of cations in the film ($\text{cm}^2 \text{s}^{-1}$), A is the electrode area, v is the potential scan rate (V s^{-1}), and i_p is the peak current.

Indeed for thin films and small scan rates (if finite diffusion occurs within the film), thin layer behavior predominates and the peak current is proportional to v according to the thin film equation.

The relationship between the peak current and scan rate may be described as follows:⁴²

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

where Γ , ν , A , and I_p are the surface coverage of the electrode, the scan rate, the electrode area, and the peak current, respectively. At scan rates higher than 200 mV s^{-1} , the anodic and cathodic peak currents were linearly proportional to the square root of the scan rate, which is expected for a diffusion controlled electrode process.

The surface coverage of the NBHCF film on the electrode, Γ , was determined from the area under the anodic voltammogram of the NBHCF film electrode:³⁶

$$\Gamma = Q/nFA \quad (2)$$

where n and F are the number of electrons transferred in the surface redox reaction and Faraday constant, respectively. The surface coverage was calculated as the efficient cross-sectional area of the electrode only and does not reflect the actual amount of NBHCF per area of CPE. In the present case, the surface coverage, Γ , was estimated at $2.0 \times 10^{-8} \text{ mol cm}^{-2}$.

The stability of the NBHCF modified electrode was examined by repetitive scans in a 0.2 M KOH solution. In the first few scans, the peak current decreases on continuous scanning. Then negligible variation in height and separation of cyclic voltammetric peaks was observed. The NBHCF modified electrode was stable under repeated CV scanning. The response of the modified electrode decreased 10% after 100 cycles. Furthermore, there was no loss of redox activity after storing the modified electrode in air for 2 weeks.

The morphology of NBHCF precipitate particles was determined by scanning electron microscopy (SEM). The scanning electron micrographs were used to evaluate the size of NBHCF particles prepared from the reaction between of NB and potassium HCF. As can be seen, the particles had average diameters of between 500 and 1000 nm (Figure 3).

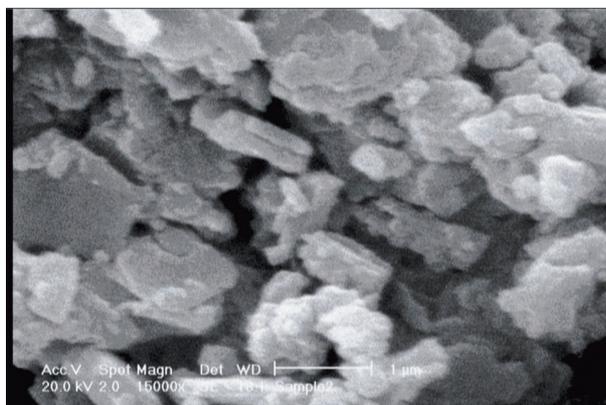


Figure 3. SEM micrographs of NBHCF.

Electrocatalytic oxidation of hydrazine

Cyclic voltammetric studies

Electrocatalytic oxidation of hydrazine at the NBHCF-CPE electrode immersed in a 0.2 M KOH supporting solution was studied using the cyclic voltammetric method. The potential was scanned from -0.2 to 0.6 V vs. SCE. In this potential range, no peak current was observed on the unmodified electrode in either the presence or absence of hydrazine in the electrolyte solution used. Cyclic voltammograms of the CPE and NBHCF-CPE electrode in both the absence (curve a,c) and presence of 50 mM hydrazine (curve b, d) are shown in Figure 4. Upon the addition of 50 mM hydrazine, an enhancement in the anodic peak current was observed and the cathodic peak current decreased significantly (Figure 4, curve c), a result that is typical for mediated oxidation. The anodic peak current was found to increase linearly with increasing concentration of hydrazine in the range of 2-70 mM (data not shown).

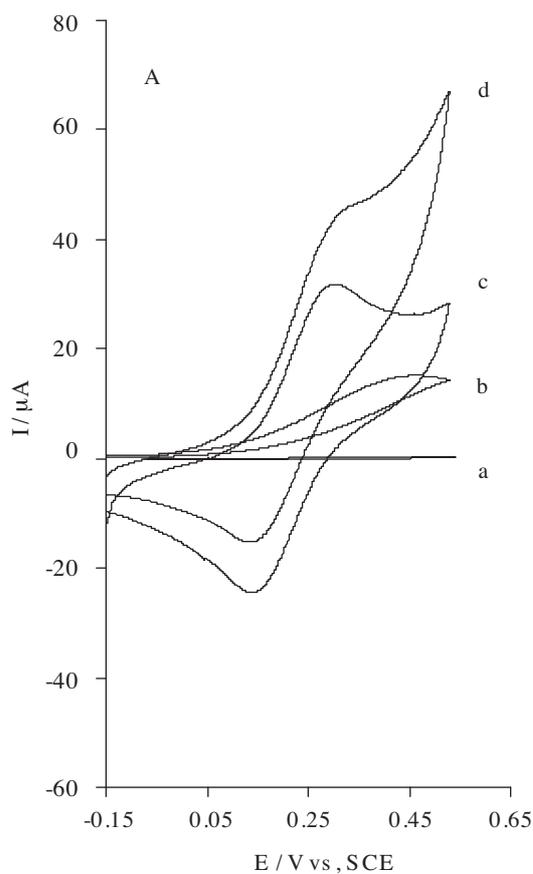


Figure 4. Cyclic voltammograms of a NBHCF electrode in 0.2 M KOH using a scan rate of 20 mV s^{-1} (a) bare CPE in the presence of 50 mM hydrazine (b) NBHCF -CPE in the absence and (c) in the presence of 50 mM hydrazine.

Differential pulse voltammetry (DPV) studies

DPV was used to examine the electrochemical behavior of the NBHCF-modified CPE since it is one of the most sensitive electrochemical techniques. Figure 5 shows the effect of changing the hydrazine concentration during the application of DPV with the NBHCF-CPE. The height of the anodic peak increased with increasing concentrations of hydrazine. The inset in Figure 5 reveals a linear relationship between I_{pa} and hydrazine concentration within a range of 0.1-0.6 mM; with a calculated correlation coefficient (R) of 0.9984. The precision of the DPV method for measuring hydrazine was tested on solutions with a concentration of 0.1 mM ($n = 4$) prepared using the standard addition method. On any given day, this analysis revealed a 2.50% relative standard deviation (R.S.D.). Furthermore, multi-day experiments (over 4 days) were also found to have excellent precision with a R.S.D. of 3.9%. At all times, the electrodes were stored at room temperature.

Hydrodynamic amperometry studies

Hydrodynamic amperograms (HDAs) were tested for a 2.0 mM solution of hydrazine using different applied potentials. The applied potential was 0.4 V, in accordance with the result of HDA. When the applied potential

was lower than 0.20 V, the results indicated an absence of electrocatalytic oxidation. In contrast, when the potential was greater than 0.40 V, the peak currents for the oxidation of hydrazine increased quickly with increasing applied potential. When the potential was greater than 0.50 V, however, baseline values were found to increase considerably. From these data, 0.40 V was chosen as the optimal detection potential for obtaining suitable signal/noise ratios. Since HDA conducted with stirring of the test solution was associated with a much higher current sensitivity, this technique was used for the quantification of low concentrations of hydrazine. The linear response using this method was determined to fall within a hydrazine concentration range of 0.1-6.0 mM and the detection limit was 40 μM when the signal to noise ratio was 3/1. When the modified electrode was examined for its stability in the presence of 2.0 mM hydrazine, a minor decrease in response time was detected following 10 min of reaction time (Figure 6).

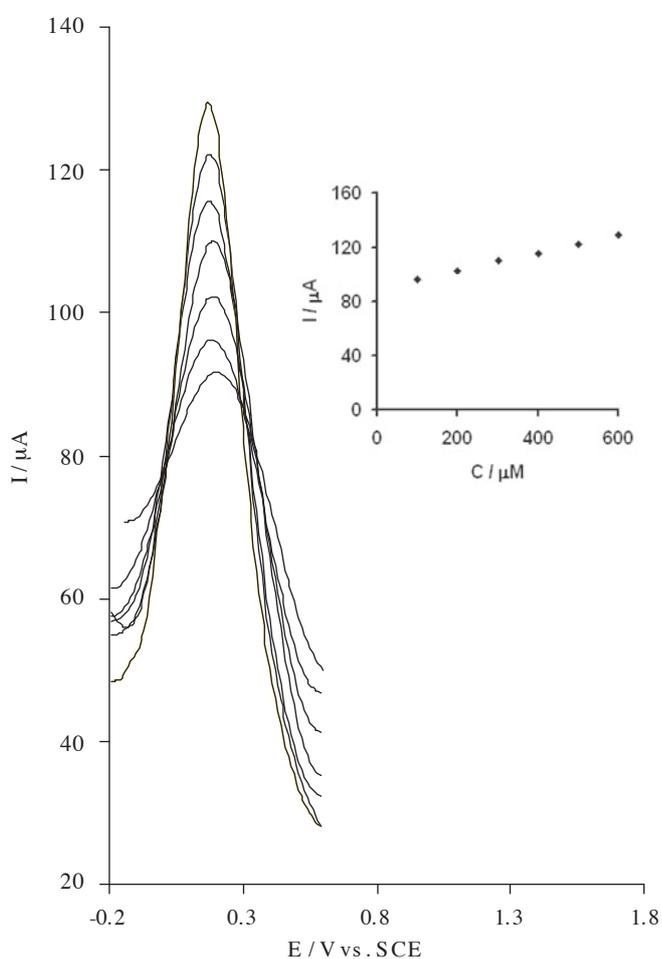


Figure 5. Differential pulse voltammetry (DPV) applied for different concentrations of hydrazine in solution (0.1, 0.2, 0.3, 0.4, 0.5, 0.6 mM). (**Inset**) calibration curve of hydrazine over a concentration range 0.1 to 0.6 mM, using 0.2 M KOH as supporting electrolyte.

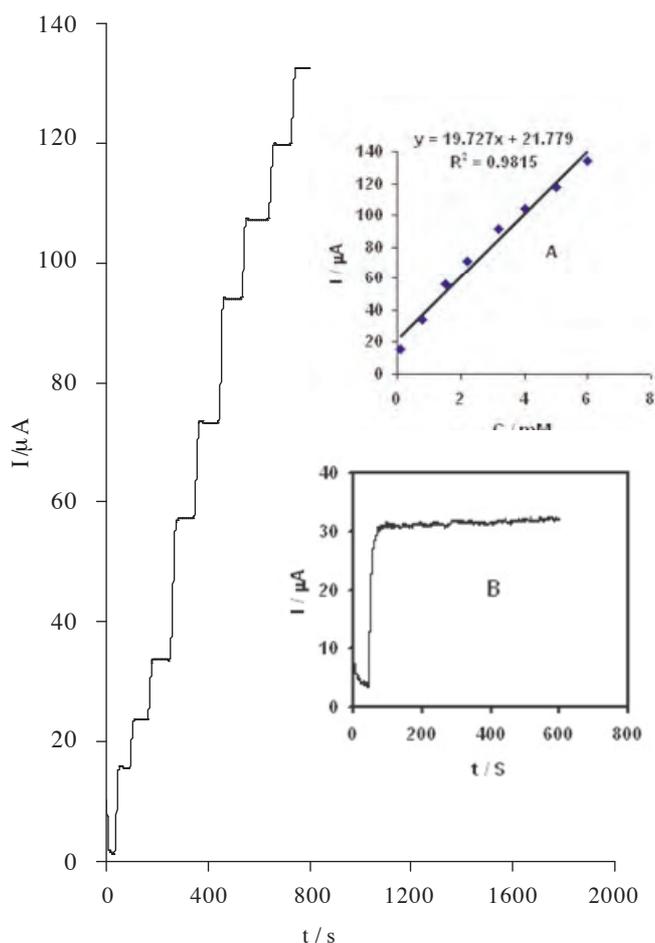


Figure 6. Hydrodynamic amperograms of the NBHCF-CPE following addition of hydrazine to a stirred supporting electrolyte solution of 0.2 M KOH. **Inset A** current vs. concentration of hydrazine curve. **Inset B** of this figure shows the stability of the response to 2.0 mM hydrazine on NBHCF-CPE in 0.2 M KOH.

Chronoamperometric studies Chronoamperometry may be used for the electrochemical investigation of chemically modified electrodes. In using this technique, 2 potential steps of -0.10 and 0.40 V were applied for forward and reverse chronoamperometry of a NBHCF-modified CPE with a surface coverage of 2×10^{-8} mol cm $^{-2}$ in both the absence and presence of 4 mM hydrazine. For an electroactive material with diffusion coefficient, D , the current corresponding to the electrochemical reaction (under diffusion control) is described by Cottrell's Law:⁴²

$$I = nFAC^{\circ}D^{1/2}\pi^{-1/2}t^{-1/2} \quad (3)$$

where D and C° are the diffusion coefficient (cm 2 s $^{-1}$) and bulk concentration (mol cm $^{-3}$) respectively. The plot of I versus $t^{-1/2}$ is linear, and from the slope the value of D may be determined. The mean value of the D of hydrazine was found to be 5.3×10^{-5} cm 2 s $^{-1}$, which is in good agreement with values reported from other investigators.^{43,44}

Conclusion

This paper describes a novel Prussian Blue analogue, Nile-Blue hexacyanoferrate (NBHCF), that remains stable in 0.2 M KOH. Experimental results have shown that this NBHCF modified electrode was stable in alkaline solutions and exhibited electrocatalytic activity for the oxidation of hydrazine. The detection limit of this sensor was 40 mM and hence it can be used as an amperometric sensor. The sensor was found to be stable with no loss of redox activity even after the prepared electrode was aged in air for 2 weeks.

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