



# Selective electrooxidation of uric acid in presence of ascorbic acid at a room temperature ionic liquid/nickel hexacyanoferrate nanoparticles composite electrode

R. Suresh Babu<sup>a</sup>, P. Prabhu<sup>a</sup>, S. Sriraman Narayanan<sup>a,b,\*</sup>

<sup>a</sup> Department of Analytical Chemistry, School of Chemical Sciences, University of Madras, Guindy Campus, Chennai 600 025, Tamil Nadu, India

<sup>b</sup> National Centre for Nanoscience and Nanotechnology, University of Madras, Guindy campus, Chennai 600 025, Tamil Nadu, India

## ARTICLE INFO

### Article history:

Received 30 April 2011

Received in revised form 5 August 2011

Accepted 12 August 2011

Available online 22 August 2011

### Keywords:

Room temperature ionic liquid

Uric acid

Nickel hexacyanoferrate nanoparticle

Cyclic voltammetry

## ABSTRACT

A novel amperometric sensor for the determination of uric acid was fabricated using room temperature ionic liquid and nickel hexacyanoferrate nanoparticle composite which was immobilized on paraffin wax impregnated graphite electrode. The nickel hexacyanoferrate nanoparticle was characterized by UV–vis, X-ray diffraction and field emission scanning electron microscopy. The electrochemical behavior of the modified electrode was investigated in detail by electrochemical impedance spectroscopy, cyclic voltammetry and differential pulse voltammetry. Various experimental parameters influencing the electrochemical behavior of the modified electrode were optimized by varying the supporting electrolyte, scan rate and pH. The apparent electron transfer rate constant ( $K_s$ ) and charge transfer coefficient ( $\alpha$ ) of the modified electrode were found to be  $1.358(\pm 0.02)$  cm/s and 0.65, respectively from cyclic voltammetry. The sensor exhibited an excellent electrocatalytic activity towards the oxidation of uric acid. The interference from ascorbic acid was easily overcome by coating the modified electrode with PEDOT layer. Under optimal condition, the determination range for uric acid is from  $1.0 \times 10^{-6}$  M to  $2.6 \times 10^{-3}$  M and the detection limit was  $3.3 \times 10^{-7}$  M ( $3\sigma$ ). The proposed method has been used for the determination of uric acid in human urine samples.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, room temperature ionic liquids (RTILs) are attracting immense interest in the area of electrochemistry for their relatively large potential windows, outstanding electrochemical stability, and extremely high ionic conductivity [1,2]. In the field of electroanalytical chemistry, the applications of RTILs are mainly on two aspects. One is that RTILs are used as the supporting liquid or solid electrolytes [1,3,4]. Another interesting application is to incorporate RTILs for fabrication of chemical sensors and biosensors. To date, RTIL based carbon paste electrodes or electrodes modified with RTIL incorporated composites are well documented [5]. Among them, the combination of RTILs with conventional matrices, such as, agarose, carbon materials, gelatin, sol–gel-based silica matrices, Nafion and gold nanoparticles, have gained special attention for creating unique materials [5]. It has been proved that the incorporation of RTILs can increase sensitivity and allow efficient direct electron transfer in various proteins/enzymes. Microdroplet and thin film deposits of an ionic liquid, 1-methyl-3-(2,6-(S)-

dimethylocten-2-yl)-imidazolium tetrafluoroborate ( $\text{MDIM}^+\text{BF}_4^-$ ) on electrode surface was studied in order to assess the ability of aqueous ions to partition into the ionic liquid [6].

Recently, there are number of reports on the use of RTILs as binders in electrode fabrication. The formation and possible electrochemical applications of molecular films of water-miscible imidazolium-based RTILs on glassy carbon (GC) electrodes have been described [5]. These molecular films are found to possess striking electrochemical properties such as electrocatalysis for oxidation of ascorbic acid (AA) and the capability to facilitate direct electron transfer in HRP. Direct electrochemistry of hemoglobin (Hb) and selective determination of dopamine in the presence of AA and uric acid (UA) at the viscous carbon nanotubes/RTIL gel modified GC electrode have been reported [7,8]. Later, it has been noted that combining RTIL with graphite powder is also a successful approach [9]. A carbon paste modified electrode using graphite powder with 1-octylpyridinium hexafluorophosphate (OPFP) as a binder and its use for the detection of some electroactive molecules has been reported [10,11].

A variety of mediators ranging from organic molecules to inorganic complexes have been applied for the construction of chemically modified electrodes. Among the various mediators used for electrode modification, solid metal hexacyanoferrates

\* Corresponding author. Tel.: +91 44 22202717; fax: +91 44 22352494.  
E-mail address: [sriraman55@yahoo.com](mailto:sriraman55@yahoo.com) (S.S. Narayanan).

have attracted the attention of electrochemists as excellent electron transfer mediators. These materials show interesting redox chemistry that is accompanied by changes in their electrochromic, electroanalytical, ion-exchange, and electrocatalytic properties [12–16]. Currently we are involved in the development of chemically modified electrodes based on metal hexacyanoferrate nanoparticles and RTIL. The preliminary investigation has demonstrated that such an electrode is thermally stable with high conductivity, and with good stability. A nickel hexacyanoferrate nanoparticle (NiHCF-NP) modified electrode using RTIL as binder may be expected to present good electrocatalytic performance towards the oxidation of compounds such as UA.

UA is an end product from purine derivatives in human metabolism. The assay of UA in body fluids (e.g. serum and urine) is a clinically valuable diagnostic indicator [17]. The presence of elevated UA levels is a sign of gout, hyperuricemia, or Lesch–Nyhan syndrome [18]. Similarly, elevated UA levels are related to other conditions including increased alcohol consumption, obesity, diabetes, high cholesterol, kidney disease, and heart diseases. Many epidemiological studies have suggested that serum UA is also a risk factor for cardiovascular disease [19]. A number of techniques have been reported for UA detection which includes chromatography [20,21], electrophoresis [22,23], mass spectrometry [24], enzymatic and colorimetric methods [25,26], chemiluminescence [27] and fluorometric method [28]. Electrochemical methods offer a better analytical platform which can exhibit a higher selectivity and sensitivity than other commonly employed methods and have the inherent advantage of low cost and rapid sensing time [29,30]. Electrochemical detection of UA may provide an inexpensive and rapid screening technique for both laboratory and field analysis [31–33].

In the present work, we report the utilization of RTIL and NiHCF-NP as components of modifying paraffin wax impregnated graphite electrode (PIGE) for electrocatalytic oxidation and amperometric determination of UA. Simple coating method was applied to immobilize RTIL–NiHCF-NP-Gel onto the surface of the PIGE. The electrochemical characterization of the modified electrode was studied in various supporting electrolytes, pHs, and different scan rates. The modified electrode has good sensitivity, rapid response time, reproducibility, remarkable stability and low detection limit. The application of the modified electrode towards the quantification of UA in urine samples was found to be promising.

## 2. Experimental

### 2.1. Apparatus

UV–visible absorption spectrum (UV–vis) was obtained with the fiber-optic spectrometer (Ocean Optics, Inc, Florida, USA) with a DT lamp. X-ray diffraction (XRD) analysis was performed on a Bruker model D8 using Cu K $\alpha$  radiation. FE-SEM image of the electrode surface was obtained on SU6600 field emission scanning electron microscopy (FE-SEM) (HITACHI, Japan).

Electrochemical measurements were performed with a CHI 660B electrochemical workstation (CH Instruments, USA) controlled by a personnel computer. Three electrode system was employed in this study. A platinum wire and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. All potentials were referred to the latter. The modified electrode employed as the working electrode was prepared according to the procedure described below. A magnetic Teflon stirrer provided the convective transport during the amperometric measurements. All the experiments were performed at room temperature.

### 2.2. Reagents

1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF<sub>4</sub>) was purchased from Alfa Aesar. UA was obtained from HIMEDIA Laboratories Pvt. Ltd., India. Potassium hexacyanoferrate, nickel chloride and potassium chloride were of analytical grade. pH was varied using 0.1 M HNO<sub>3</sub> and 0.1 M NaOH solutions. All other reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with doubly distilled water.

### 2.3. Preparation of nickel hexacyanoferrate nanoparticle (NiHCF-NP)

NiHCF-NP was synthesized by dropwise addition of 35 mL of a 0.01 M aqueous solution of NiCl<sub>2</sub> to a 35 mL solution of 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> containing 0.05 M KCl under stirring [16]. After complete addition, the liquid was vigorously agitated for 5 min and then immediately subjected to filtration using a 0.4  $\mu$ m Millipore cellulose filter membrane. The retentate was continuously washed with water and then collected after filtration and dried overnight in vacuum at room temperature to get a powdered compound.

### 2.4. Electrode preparation

About 20 mg NiHCF-NP mixed with 10  $\mu$ L EMIMBF<sub>4</sub> were ground with an agate mortar for about 10 min, and a gel was obtained. PIGE with a circular surface diameter of 3 mm prepared as reported [15] was used for electrode modification. One end of the electrode was carefully polished on a smooth surface and with 0.5  $\mu$ m alumina, washed with distilled water and dried in air. Then, the polished surface was coated with RTIL–NiHCF-NP-Gel by mechanical transfer. Finally, the gel on the electrode surface was spread with a spatula to have a thin gel film on the PIGE surface, which was used as the working electrode. All voltammograms of the modified electrodes were recorded after the electrode has reached equilibrium with the background electrolyte. For comparison, NiHCF-NP modified PIGE was also prepared through mechanical immobilization of NiHCF-NP and RTIL modified PIGE was prepared with RTIL by drop casting on the PIGE surface.

## 3. Results and discussion

### 3.1. Characterization of the NiHCF-NP and RTIL–NiHCF-NP-Gel modified PIGE

The NiHCF-NP was characterized by UV–vis spectroscopy. The UV–vis spectrum of NiHCF-NP exhibits a strong absorbance at 290 nm and a broad absorbance around 400 nm. This observation is in consistent with earlier reports [16], which indicate the formation of NiHCF-NP. The powder XRD analysis was used to demonstrate the formation of NiHCF-NP. As shown in Fig. 1A, four peaks were observed at 17.4°, 24.7°, 35.1°, 39.4°, which can be assigned to the diffractions of (2 0 0), (2 2 0), (4 0 0), (4 2 0) planes demonstrating the face centered cubic (fcc) structure of NiHCF and the peak positions are identical to NiHCF pattern [JCPDS card, file no. 750037]. The XRD peaks are broad, indicating the existence of crystallites of nanometer dimensions. The average crystalline size, which was determined from the half width of the diffraction peaks using the Debye–Scherrer formula, was approximately 20 nm.

The distribution of the NiHCF-NP on the electrode surface is shown by FE-SEM image (Fig. 1B). The average sizes of the NiHCF-NP are in the range of 20–40 nm in diameter. The size of the NiHCF-NP in FE-SEM was almost similar to XRD results. The NiHCF-

Download English Version:

<https://daneshyari.com/en/article/601124>

Download Persian Version:

<https://daneshyari.com/article/601124>

[Daneshyari.com](https://daneshyari.com)