Electrodeposition of Copper Nano-clusters at a Platinum Microelectrode for Trace Nitrate Determination

Yang Li\textsuperscript{a,b}, Jizhou Sun\textsuperscript{a}, Chao Bian\textsuperscript{a}, Jianhua Tong\textsuperscript{a} and Shanhong Xia\textsuperscript{a,*}

\textsuperscript{a}State Key Laboratory of Transducer Technology, Institute of Electronics, Chinese Academy of Sciences, Beijing, 100190, P.R.China
\textsuperscript{b}Graduate University of Chinese Academy of Sciences, Beijing, 100190, P.R.China

Abstract

Copper nano-clusters were electrodeposited onto a platinum microelectrode by cyclic voltammetry method to fabricate an electrochemical sensor for trace nitrate determination. The freshly deposited copper layer were characterized by scanning electron microscopy (SEM). Then, electrochemical response of the porous copper nano-clusters morphological layer under mildly acidic conditions ($\text{pH}=3$) was characterized by linear sweep voltammetry. The preliminary experimental results reveal that the microelectrode surface modified by cyclic voltammetry electrodeposition was porous and has a larger effective surface area, which shows marked sensitivity for trace nitrate ions within the concentration range from 1.25 to 300 $\mu$molL$^{-1}$.

© 2010 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Nitrate determination; Copper nano-clusters; Cyclic voltammetry electrodeposition; Platinum microelectrode;

1. Introduction

Nomenclature

|$i_p^*$| the normalized sensitivity |
|$i_p$| the peak reduction current (A) |
|$n$| the number of electrons transfer in the reduction step |
|$A$| the surface area of electrode (cm$^2$) |
|$v$| the potential sweep rate (Vs$^{-1}$) |
|$C_0^*$| the bulk concentration of nitrate (M) |

* Corresponding author. Tel.: +86-10-58887180 ; fax: +86-10-62535627 .
E-mail address: shxia@mail.ie.ac.cn .
Nitrate has a widespread distribution within environmental, food, industrial and physiological systems. Lots of studies have proved that excessive nitrate can present both environmental and physiological problems \cite{1}. Due to the possible dangers associated with nitrate, the World Health Organization (WHO) recommends that the nitrate levels (as N-NO$_3^-$) in potable water should not exceed 0.8 mmol L$^{-1}$ (or 11 mg L$^{-1}$). The US Environmental Protection Agency (EPA) has also imposed a limit of 0.7 mmol L$^{-1}$ (or 10 mg L$^{-1}$) nitrate on drinking water. So it is clear that monitoring nitrate concentration in aqueous solutions is extremely important.

Electrochemical techniques have been widely used in nitrate determination. But due to slow kinetics of charge transfer, direct reduction of nitrate on bare unmodified electrodes is usually difficult. The surface cumulative passivation effects of bare electrodes will also lead to low sensitivity and irreproducibility. So to improve the selectivity and sensitivity in the process of quantifying nitrate, researchers intend to modify the electrodes with sensitive materials prior to electrochemical analysis. A wide variety of materials have been investigated, such as copper, silver, platinum, palladium, thallium\cite{1}, doped-polypyrrole nanowires\cite{2,3} and nitrate reductase enzymes\cite{4}. Since the electrodeposition of copper is both inexpensive and simple, several literatures have proved that copper is an effective material for electroanalytical determination of nitrate\cite{5-8}.

However, the majority of these investigations have often focused on obtaining active copper surface by fixed potential deposition method. Few applications have been paid attention to employing different electrodeposition methods to improve the sensitivity of the electrode response for nitrate determination. For this purpose, the work reported herein mainly presents the characterization of a porous copper nano-clusters morphological layer developed by cyclic voltammetry electrodeposition and its electrochemical response towards nitrate within a concentration range (10–300 μmol L$^{-1}$) which is relevant to a number of analytical applications. The primary experimental results showed that the modified electrode has a marked sensitivity for trace nitrate determination.

2. Experimental section

2.1. Chemicals and materials

All solid reagents were of analytical grade and were used without further purification. Copper(II) sulphate, sulphuric acid, sodium sulphate and sodium nitrate were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd (Beijing, China). The supporting electrolyte in all experiments was a 0.1 mol L$^{-1}$ Na$_2$SO$_4$ solution, pH=3.0 (adjusted with H$_2$SO$_4$). In almost all cases the solutions were prepared by dissolving the reagents in deionised water with a resistivity of 18 M$\Omega$ cm.

2.2. Electrodes and instrumentation

An Autolab Reference-600 (Gamry, USA) bipotentiostat with data acquisition software made available by the manufacturer (Gamry Echem Analyst Version 5.50) was used for electrochemical measurements. Experiments were carried out in a conventional electrochemical cell with a three-electrode-system, including an Ag/AgCl electrode as...
the reference electrode and a microelectrode chip. The chip composed of a working electrode and a counter electrode was fabricated with platinum by photolithography and lift-off processes. Fig 1 shows the structure of the microelectrode chip. The sensitive area of the working electrode is only 1mm². All experiments were carried out at room temperature.

2.3. Electrode modification

The electrode modification was performed by cyclic voltammetry electrodeposition (50 mVs⁻¹) between 0V and -0.8V vs. SCE for 5 cycles in 0.1molL⁻¹ CuSO₄ electrolytic solutions. The cyclic voltammograms of modification process is shown in Fig 2(a). After modification process, the electrode was rinsed with deionised water, then immersed in deionised water, prepared to be used.

3. Results and discussion

The morphology of freshly deposited copper layer was examined by SEM, as shown in Fig 2(b). It was found that the surface of the microelectrode is porous and has a larger effective surface area due to the formation of copper nano-clusters. The nano-clusters were constructed by nanoparticles with an average diameter of about 100 nm and as shown in Fig 2(c).

Fig 3. Linear sweep voltammograms detailing the standard addition determination of nitrate: (a) voltammograms recorded in 0, 12.5, 25, 37.5, 50, 62.5, 75, 100, 125, 150, 200, 300μmolL⁻¹ NaNO₃ solutions(up to down); (b) the corresponding calibration plots of peak current values. Potential scan rate: 50mVs⁻¹.

Fig 3(a) shows the linear sweep voltammograms of the microelectrode modified by cyclic voltammetry electrodeposition for consecutive additions of NaNO₃ solution into supporting electrolyte. Fig 3(b) shows calibration plots of peak current values measured in the voltammograms(Ec=-450mV) as a function of nitrate concentration in the range of 12.5-300 μmolL⁻¹, which is very important for water intended for human consumption[1]. The plot of
peak current values as a function of nitrate concentration in the range yielded straight lines: $y = -0.04x - 4.4089$ \( R^2 = 0.9905 \).

Fig 3(a) also indicates that after addition of NaNO₃ solution into supporting electrolyte there is a sharp reduction peak for nitrate reduction at \( E_1 = -450 \text{mV} \). This reduction potentials is significantly less negative than those reported in other literatures (\( E_2 = -500 \text{mV} \))[6,7], which indicates that copper nano-clusters are more effective electrocatalyst in facilitating nitrate reduction.

To verify whether microelectrode modified by cyclic voltammetry electrodeposition exhibit higher sensitivity, a normalized sensitivity, \( i_p^* \), is defined as[9]:

\[
i_p^* = \frac{i_p}{nA v^{1/2} C_o^{1/2}}
\]

Table 1 shows the normalized sensitivity, \( i_p^* \), calculated for nitrate reduction in different electrochemical systems with the experimental parameters obtained from literatures. When copper was used as the working electrode, let \( n = 8 \)[7], unless literature notes otherwise. It is found that the microelectrode described here shows greater sensitivity than other work.

Table 1. Normalized peak current for reduction of nitrate

<table>
<thead>
<tr>
<th>( i_p^* )</th>
<th>( v(\text{Vs}^{-1}) )</th>
<th>( A(\text{cm}^2) )</th>
<th>Supporting electrolyte</th>
<th>Working electrode</th>
<th>Literatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.55</td>
<td>0.05</td>
<td>0.01</td>
<td>0.1 M NaSO₄(pH=3.0; H₂SO₄)</td>
<td>Copper-plated Platinum Microelectrode</td>
<td>This paper</td>
</tr>
<tr>
<td>1.3</td>
<td>0.002</td>
<td>1.2</td>
<td>0.5M H₂SO₄+0.1mM KCl+0.01M CuSO₄</td>
<td>Copper-plated graphite</td>
<td>1991, [5]</td>
</tr>
<tr>
<td>2.85</td>
<td>0.01</td>
<td>0.07</td>
<td>0.1M NaSO₄+0.1M HCl</td>
<td>Copper-plated glassy carbon</td>
<td>2000, [6]</td>
</tr>
<tr>
<td>2.08</td>
<td>0.005</td>
<td>0.2826</td>
<td>0.5M H₂SO₄</td>
<td>Graphite modified with doped-polypyrrole nanowires</td>
<td>2006, [3]</td>
</tr>
<tr>
<td>0.79</td>
<td>0.1</td>
<td>0.07</td>
<td>0.1 M NaSO₄(pH=2.0; H₂SO₄)</td>
<td>Copper wire</td>
<td>2007, [7]</td>
</tr>
<tr>
<td>2.47</td>
<td>0.01</td>
<td>0.00196</td>
<td>0.01M NaOH</td>
<td>Silver disk electrode</td>
<td>2007, [9]</td>
</tr>
</tbody>
</table>

Acknowledgements

The authors gratefully acknowledge financial support from the National Basic Research Program of China (973 Program) (No. 2009CB320300) and Major projects on control and rectification of water body pollution (No. 2009ZX07527-007).

References