Highly sensitive and selective determination of thiocyanate using gold nanoparticles surface decorated multi-walled carbon nanotubes modified carbon paste electrode

Abbas Afkhami*, Farzaneh Soltani-Felehgari, Tayyebeh Madrakian

Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

ARTICLE INFO

ABSTRACT

Gold nanoparticles and multi-walled carbon nanotubes were used to fabricate a modified electrode, as a highly sensitive and selective voltammetric sensor, for the determination of thiocyanate. A fast and easy method for the fabrication of gold nanoparticles/multi walled carbon nanotube/carbon paste electrode (GNPs/MWCPE) by cyclic voltammetry was used. Scanning electron microscopy (SEM) image demonstrated that the gold nanoparticles deposited on MWCNTs/CPE, with an average size of 30 nm. By combining the benefits of GNPs/MWCNTs and CPE, the resulted modified electrode exhibited outstanding electrocatalytic activity in terms of thiocyanate oxidation by giving much higher peak currents than those obtained for the unmodified CPE and also the MWCNTs-modified electrode. The effects of various experimental parameters on the voltammetric response of thiocyanate were investigated. At the optimum conditions the sensor has a linear response in the 0.01–200.0 μmol L^{-1} concentration range, a very good detection sensitivity (2.9046 μA L μmol^{-1}), and a low detection limit of 5×10^{-3} μmol L^{-1} of thiocyanate. The proposed electrode was used to the determination of SCN$^-$ in saliva, urine and water samples and the results were found to be in good agreement with the values obtained by standard method.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Thiocyanate (SCN$^-$) is present as a normal constituent in mammalian tissues and body fluids [1]. It is also present in industrial waste-waters, pesticide residues and organism metabolites. Since thiocyanate is an end product of detoxification of hydrogen cyanide, is present in human urine, plasma and saliva. Higher concentrations of this ion arise from tobacco smoke [2,3]. Therefore, its concentration in human urine, serum and saliva can provide a useful probe for distinguishing between smokers and non-smokers [4]. If the content of thiocyanate in the body is a little higher than normal, the protein dialysis will be affected and it may even results in coma. It has been found that there is a correlation between the blood cyanide, the plasma thiocyanate, and the salivary thiocyanate [5]. Therefore, the determination of the SCN$^-$ concentration at low levels especially in food, biological and water samples is important.

Various methods, such as spectrophotometry [6,7], spectrofluorimetry [8], Raman spectroscopy [9], capillary zone electrophoresis [10], Aldridge method [11], gas chromatography [12], electrochemistry [13], photokinetic voltammetry [14], ion chromatography [15], and potentiometry based on ion-selective electrodes (ISEs) [16–23], have been reported for the determination of thiocyanate concentration in various samples. However, these methods have disadvantages such as the toxicity of used reagents, time-consuming extraction processes and the presence of serious interferences. Therefore, it is essential to look for new materials and methods with high sensitivity and efficiency for the detection of SCN$^-$. Electrochemical methods are often favored over others because they are faster, cheaper and simpler [24].

Carbon paste electrode (CPE), which was made up of carbon particles and an organic liquid, has been widely applied in the electroanalytical community due to its low cost, ease of fabrication, high sensitivity for detection and renewable surface. Lately, to improve the sensitivity, selectivity, detection limit and other features of CPE, chemically modified carbon paste electrodes (CMCPEs) have been used. CMCPEs are prepared by the addition of a suitable modifier to carbon paste. The operation mechanism of such CMCPEs depends on the properties of the modifier materials used to import selectivity and sensitivity towards the target species. Initially, non-conductive reagents, such as mineral oil or paraffin oil were used as binders [25,26]. Since their discovery in 1991 [27], with their exceptional electrical, chemical and mechanical properties, carbon nanotubes (CNTs) have become extremely attractive over the past years in the task of chemical sensors and biosensors [28–33].

Metal nanoparticles have received considerable attention in recent years. They have unique chemical, electrical and optical

* Corresponding author. Tel.: +98 811 8272404; fax: +98 811 8272404.
  E-mail address: afkhami@basu.ac.ir (A. Afkhami).

properties due to their size-dependent properties and quantum size effects. They are very promising for practical applications in many diverse fields, such as electronic nano devices, molecular catalysts, multifunctional reagents and biosensors [34–36]. Gold nanoparticles (GNPs) have attracted considerable attention in electrochemical fields because of their advantages of catalysis, mass transport, high effective surface area and control over surrounding environment [37–41].

In continuation of our previous works on the construction and application of GNPs modified CPE to the analysis of different chemical species [26,42], we report construction and application of an electrochemical sensor based on GNPs for the determination of thiocyanate in different samples. The sensor was constructed by decoration of gold nanoparticles at the multi-walled carbon nanotubes modified carbon paste electrode (MWCNTs/CPE) surface by cyclic voltammetry. The construction method was simpler and faster as compared to our previously reported method [26,42]. The proposed sensor displays a low detection limit and high selectivity and sensitivity to thiocyanate determination in real samples. Since the limit of detection of the proposed sensor is better than that for some reported methods [4,43–45], and it is several orders of magnitude lower than the thiocyanate concentration in biological samples [1] and also because of high selectivity and sensitivity of the method, the developed electrode was used to the square wave voltammetric (SWV) determination of trace amounts of thiocyanate in real samples, such as the saliva and urine samples of smokers and non-smokers.

The modifier combined the unique electronic properties of MWCNTs and attributes of gold nanoparticles such as their high surface-to-volume ratio, high catalytic efficiency, good biocompatibility and chemical stability, thus, a synergistic effect occurred in GNP-MWCNT/CPE hybrids for exerting their enhanced electrocatalytic capabilities.

2. Experimental

2.1. Materials and apparatus

All Reagents and materials were of analytical grade from Merck or Aldrich. All the solutions were prepared using double-distilled water. Britton–Robinson (B–R) buffer solutions $(4.0 \times 10^{-2}\,mol\,L^{-1})$ of pH 2.0–9.0 $(CH_3COOH + H_3BO_3 + H_3PO_4)$ were used as the supporting electrolyte. The pH was adjusted using $0.2\,mol\,L^{-1}$ NaOH. A Metrohm Model 827 pH lab (Herisau, Switzerland) pH-meter with a combined glass electrode was used for pH measurements. A magnetic stirrer (PAR-305) with a Teflon-coated magnet was used to provide the convective transport during the electro-deposition and preconcentration step. The size and morphology of the electrode surface was characterized by a scanning electron microscope (SEM-EDX, XL30 and Philips Netherland). Voltammetric systems were conducted using a potentiostat/galvanostat (Autolab PGSTAT302N) and it was controlled by a computer using Nova version 1.7 software. Three-electrode cell systems were used to monitor the cyclic and square-wave voltammograms. A saturated Ag/AgCl electrode, a platinum wire and a modified carbon paste electrode were used as the reference, auxiliary and working electrodes, respectively.

2.2. Pretreatment of multi-walled carbon nanotube materials and modified carbon paste electrode

A pretreatment of the CNTs is usually necessary to eliminate graphitic nanoparticles, amorphous carbon, metallic impurities, and/or to improve the electron transfer properties and/or to allow further functionalization [46]. The preparation of multi-walled

carbon nanotubes modified carbon paste electrode (MWCNTs/CPE) with composition of 10.0% (w/w) MWCNTs, 65.0% (w/w) graphite powder and 25.0% (w/w) paraffin oil was performed as described in our previous work [42].

After fabrication of MWCNTs/CPE, the electrode tips were smoothed manually with clean paper and then at a plane glass surface to produce a flat surface.

The GNPs modified MWCNTs/CPE (GNPs/MWCNTs/CPE) was obtained by CV scanning from 0.700 to 0.000 V in a $0.1\,mol\,L^{-1}$ KNO$_3$ deaerated solution containing $0.5\,mmol\,L^{-1}$ HAuCl$_4$ (pH 3) at a scan rate of $50\,mV\,s^{-1}$ for 15 scans. Then, the modified electrode was washed with doubly distilled water and dried carefully.

2.3. Voltammetric measurements

For all measurements, the three electrodes were immersed in a 50 mL beaker containing the solution. The solution was stirred using a magnetic stirrer. The pH of the test solutions containing thiocyanate was adjusted at 5.0 by B–R buffer. In cyclic voltammetric measurements, the potential was swept from 0.400 to 1.200 V vs. saturated Ag/AgCl with a scan rate of $100\,mV\,s^{-1}$. The square wave voltammograms (SWVs) were achieved at an initial potential of 0.700 V and a final potential of 1.200 V vs. saturated Ag/AgCl, with pulse amplitude of 0.110 V. The square wave anodic signal that was obtained with applying a potential of 0.100 V vs. saturated Ag/AgCl as a collection potential was used for the determination of thiocyanate concentration.

2.4. Sample preparation

Saliva samples from smokers and non-smokers were collected and centrifuged for 3 min with a rate of 3000 rpm. After appropriate dilution, the samples analyzed according to the analytical procedure described above.

The urine samples were taken from smoker and non-smoker individuals immediately before the experiments. Acetonitrile removes proteins more effectively; the addition of 1–1.5 vol. of acetonitrile is sufficient to remove the proteins. After vortexing for 30 s, the mixture was then centrifuged for 10 min at 3000 rpm to separate urine protein residues and the supernatant was taken carefully. Appropriate volumes of this supernatant were transferred into a 50.0 mL volumetric flask and then, the samples analyzed according to the analytical procedure described above. No preparation was required for mineral and tap water samples.

3. Results and discussion

3.1. Characterization of the working electrode

Fig. 1 shows the cyclic voltammograms obtained during the electro-reduction of a $0.5\,mmol\,L^{-1}$ HAuCl$_4$ solution in $0.1\,mol\,L^{-1}$ KNO$_3$ on MWCNTs/CPE. In our study, MWCNTs/CPE was chosen as a chemically inert electrode material [47]. KNO$_3$ was employed as supporting electrolyte instead of KCl because the latter has been reported to have a negative effect with respect to Au electrodeposition by favoring a coalescence phenomenon, leading to the formation of less numerous, large-sized NPs [48]. The shape of the first voltammogram (curve 1) is consistent with that previously described under similar conditions [49,50]. The forward scan exhibits the reduction of Au(III) to Au(0) with a cathodic peak at 0.38 V, inducing the deposition of AuNPs onto the electrode surface. On the higher consecutive voltammograms, the reduction peak of Au(III) was shifted from 0.38 to 0.48 V, strengthening that Au deposition occurred preferentially on the NPs created during the first scan. This is consistent with thermodynamics which predicts an easier growth of previously formed AuNPs than a nucleation of