Fabrication and characterization of molybdenum(VI) complex–TiO$_2$ nanoparticles modified electrode for the electrocatalytic determination of L-cysteine

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Abstract: A novel voltammetric sensor for the determination of L-cysteine (L-Cys) was fabricated based on a TiO$_2$ nanoparticles/bis[bis(salicylidene-1,4-phenylenediamine) molybdenum(VI)] carbon paste electrode. The electrochemical behavior of the sensor was investigated in detail by cyclic voltammetry. The apparent electron transfer rate constant (k_s) and charge transfer coefficient (α) of the TiO$_2$ nanoparticles/molybdenum(VI) complex/carbon paste electrode (CPE) were also determined by cyclic voltammetry and found to be about 4.53 s^{-1} and 0.54, respectively. The sensor displayed good electrocatalytic activity towards the oxidation of L-Cys. The peak potential for the oxidation of L-Cys was lowered by at least 130 mV compared with that obtained at an unmodified CPE. Under optimal conditions, the linear range spans L-Cys concentrations from 1.5×10^{-6} to 1.2×10^{-3} M and the detection limit was 0.70±0.01 µM at a signal-to-noise ratio of 2. In addition, the sensor showed good stability and reproducibility.

Keywords: L-cysteine; TiO$_2$ nanoparticles; carbon paste electrode; electrocatalysis.

INTRODUCTION

Nano-sized materials have found promising technological applications in many different areas, such as microelectronic devices,[1] photocatalysis,[2] electrocatalysis,[3] biomedical applications[4] and chemical processes.[5] Nanoparticle architectures on electrode supports has attracted substantial research efforts directed to the development of bioelectrochemistry.[6] This is a great opportunity for the chemistry of nanoparticles, as the electronic properties are now tunable *via* particle

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size. With respect to the electrical properties of nanoparticles and of all kind of arrangements constructed from nanoparticles, the most important property is the amount of energy needed to add one extra electron to an initially uncharged particle. This energy is the so-called "charging energy"; it scales roughly with $1/r$ (r = radius of the nanoparticle), and it has its atomic analog in the electron affinity of a neutral atom.[7]

The chemical modification of electrodes with a suitable reagent has been widely used for analytical applications. The resulting electrodes were designed to provide the desired selective sites towards the analytes. Chemically modified electrodes (CMEs) have played an important role in studies of electrocatalysis,[8] electron transfer kinetics,[9] membrane barriers,[10] electro-organic syntheses,[11] *etc*. One of the most important electrode modification techniques involves the formation of electrocatalytic systems in which redox species capable of undergoing a rapid and reversible electrode reaction are incorporated onto the electrode surface.[3] These electrodes reduce the overpotential required for either oxidation or reduction of compounds.

L-Cysteine (L-Cys) is an important thio-containing amino acid involved in a variety of important cellular functions, such as protein synthesis, detoxification and metabolism.[12] It has been also used as a radio-protective agent, cancer indicator and is implicated in a number of pathological conditions, including Alzheimer's and Parkinson's diseases as well as autoimmune deficiency syndrome.[13] On the other hand, a deficiency of L-Cys causes many diseases, such as slowed growth in children, depigmentation of hair, edema, lethargy, liver damage, loss of muscle and fat, skin lesion and weakness.[14] Therefore, a sensitive and selective assessment of L-Cys in biological matrices and pharmaceutical preparations is highly demanded.

Electrochemical detection of thiols has been reviewed in the literatures.[15,16] Generally, the responses to thiol oxidation at unmodified electrodes usually suffer from large overpotentials or sluggish electrochemical responses.[16] The chemical modification of inert substrate electrodes with mediators offers significant advantages in the design and development of L-Cys electrochemical sensors. Therefore, biochemists and electroanalytical chemists have shown great interest in the area of modified electrodes to overcome these problems and various modified electrodes have been constructed for this purpose.[17–21]

In continuation of our studies concerning the preparation of chemically modified electrodes,[3,17,19,22–25] in the present work it was found that a TiO$_2$ nanoparticles/bis[bis(salicylidene-1,4-phenylenediamine) molybdenum(VI)] carbon paste electrode possesses high stability and good electrocatalytic activity toward the electrocatalytic oxidation of L-Cys. Cyclic voltammetry, differential pulse voltammetry and chronoamperometry were used to characterize the elec-

trochemical properties of the electrode and to investigate its electrocatalytic effect on L-Cys oxidation.

EXPERIMENTAL

Apparatus and chemicals

The electrochemical experiments were realized using a computerized potentiostat/galvanostat µAutolab type III (Eco Chemie B.V.A). A conventional three electrode cell was used with an Ag/AgCl/KCl 3.0 M, a platinum wire, and a molybdenum(VI) complex––TiO$_2$ nanoparticles modified carbon paste electrode (MCTNMCPE) as the reference, auxiliary and working electrodes, respectively. A Metrohm model 691 pH/ mV meter was used for the pH measurements.

All solutions were freshly prepared with doubly distilled water. L-Cys and other reagents were of analytical grade (Merck, Germany). Graphite powder (Merck) and paraffin oil (DC 350, Merck, density 0.88 g cm^{-3}) were used as binding agents for the graphite pastes. Phosphate buffer solutions were prepared from *ortho*-phosphoric acid and its salts in the pH range of 2.0–11.0. TiO$_2$ nanoparticles (surface area = 84 m^2 g^{-1} and particle size = 6.7 nm) and dioxomolybdenum (VI) complexes, [MoO$_2$L]$_2$, were synthesized as reported previously.[25]

Preparation of the electrode

The modified electrodes were prepared by dissolving 0.01 g of bis[bis(salicylidene-1,4-phenylenediamine) molybdenum(VI) in CH$_3$Cl and hand mixing with 95 times its weight of graphite powder and 4 times its weight of TiO$_2$ nanoparticles using a pestle and mortar. Paraffin (Dc 350, Merck) was added to the above mixture and mixed for 20 min until a uniformly wetted paste was obtained. This paste was then packed into the end of a glass tube (*ca*. 3.4 mm i.d. and 10 cm long). A copper wire inserted into the carbon paste provided for electrical contact. When necessary, a new surface was obtained by pushing an excess of paste out of the tube, which was then polished with weighing paper.

Unmodified carbon paste was prepared in the same manner but without the addition of bis[bis(salicylidene-1,4-phenylenediamine) molybdenum (VI)] and TiO$_2$ nanoparticles to the mixture. This was used for the purpose of comparison.

Procedures for sample preparation

Human blood serum. Serum was prepared by centrifuging 10 ml of blood after it had been kept in an incubator at 37 °C for 30 min. A 1.0 ml portion of serum was added to 10 ml of 0.1 M phosphate buffer (pH 8.0) in a voltammetric cell and the cyclic voltammograms were recorded.

Acetylcysteine tablets. A 20-mg portion of a finely powdered sample was dissolved in 10 ml of phosphate buffer (pH 8.0) and then 0.1 ml of sample was transferred to a 10 ml voltammetric cell containing 0.1 M phosphate buffer (pH 8.0) and the cyclic voltammograms were recorded.

RESULTS AND DISCUSSION

Electrochemistry of MCTNMCPE

The molybdenum complex was insoluble in aqueous medium and hence it could be easily incorporated into the carbon paste without concern regarding its leaching from the electrode surface. This fabrication process yielded a stable, chemically-modified electrode.

First, the electrochemical behavior of the molybdenum complex modified electrode was studied. The cyclic voltammograms for the modified electrode at different scan rates in 0.1 M phosphate buffer of pH 8.0 were recorded. The cyclic voltammograms of $[MoO_2L]_2$ in the MCTNMCPE showed an anodic and corresponding cathodic peak, whereas the unmodified carbon paste electrodes in the supporting electrolyte showed neither anodic nor cathodic peaks. Experimental investigations show that well-defined and reproducible anodic and cathodic peaks related to the Mo (VI)/Mo (V) redox system (with E_{pa} = 0.760 V, E_{pc} = = 0.58 V, E°' = 0.670 V *vs*. Ag/AgCl/KCl 3.0 M and ΔE_p = 180 mV) can be used as mediators for the electrocatalysis of some important biological compounds with a slow electron transfer. The electrode process was quasi-reversible, with ΔE_p, greater than the (59/*n*) mV expected for a reversible system. The voltammograms of a quasi-reversible system are more drawn-out and exhibit larger separation of the peak potentials compared to those of a reversible system.[26]

Cyclic voltammograms of the MCTNMCPE were recorded at different scan rates (from 20 to 900 mV s^{-1}). Figure 1A illustrates that the anodic and cathodic peak currents (I_p) were linearly dependent on *v* at scan rates in the range 30−200 mV s^{-1}. A linear correlation was obtained between peak currents and the scan rate, indicating that the redox process is not diffusion controlled. With increasing *v*, the difference between the peak potentials increased. The anodic peak potentials E_{pa} as a function of the scan rate are shown in Fig. 1B. The values of E_p were proportional to the logarithm of the scan rate for scan rates above 200 mV s^{-1}.

The equations of linear potential sweep voltammograms have been derived for any degree of reversibility of the electrochemical reaction for the following methods: surface voltammetry when both the oxidized and the reduced forms are strongly adsorbed and a Langmuir isotherm is obeyed, thin layer voltammetry and linear potential sweep coulometry. If values of ΔE_p larger than 200/*n* mV can be obtained experimentally, α and k can be easily determined using the following equations:[28]

$$E_{pc} = E° + A \ln [(1 − \alpha)/m] \tag{1}$$
$$E_{pa} = E° + B \ln [\alpha/m] \tag{2}$$

For $E_{pa} − E_{pc} = \Delta E_p$:

$$\log(k_s/s^{-1}) = \alpha \log (1−\alpha) + (1−\alpha) \log \alpha − \log (RT/nFv) − $$
$$− \alpha (1−\alpha) n_\alpha F \Delta E_p/2.3RT \tag{3}$$

where $A = RT/(1−\alpha)nF$, $B = RT/\alpha nF$ and $m = (RT/F)(k_s/n_\alpha)$.

The transfer coefficient (α) and the apparent charge transfer rate constant (k_s in s^{-1}) for electron transfer between the electrode and the molybdenum complex can be determined by measuring the variation of the peak potentials with scan rate (*v*). A graph of E_p *vs*. log (*v* / mV s^{-1}) (Fig. 1B) yields two straight lines with slopes equal to $2.3RT/\alpha n_\alpha F$ and $2.3RT/(1−\alpha)n_\alpha F$ for the cathodic and anodic

peaks, respectively. For scan rates exceeding 200 mV s^{-1}, the values of ΔE were proportional to the logarithm of the scan rate, as indicated by Laviron. Using such graphs and Eq. (3), the values of α and k_s were determined to be 0.54 and 4.53±0.30 s^{-1}, respectively, for the MCTNMCPE in the presence of 0.1 M phosphate buffer.
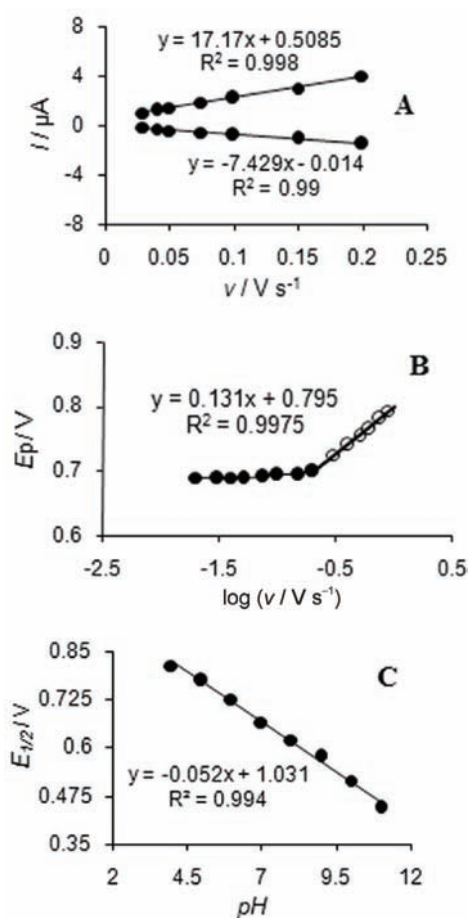

Fig. 1. A) Variation of the peak currents with scan rate; B) variation of E_p *vs.* the log v; C) plot of $E_{1/2}$ *vs.* pH for the MCTNMCPE in 0.1 M phosphate buffer solution.

The surface coverage of the electrode was approximately estimated by adopting the method used by Bard.[29] The surface concentration of molybdenum complex (Γ in mol cm^{-2}) was obtained from the integrated charges (Q) of the anodic peak as follows:

$$\Gamma_{EBNBH} = Q/nFA \qquad (4)$$

where Q is the charge from the area under the molybdenum complex anodic peak corrected for the baseline and n is the number of electrons exchanged per reactant

molecule. The surface concentration of the molybdenum complex was calculated to be 1.37×10^{-9} mol cm^{-2} for $n = 1$.

pH effect

The electrochemical response of the bis[bis(salicylidene-1,4-phenylene-diamine) molybdenum(VI)] molecule showed a strong dependence on pH. For reversible processes, the number of proton ions participating in the electrochemical reaction can be determined from the pH-dependence of the voltammetric half-wave potential. The anodic and cathodic peak potentials of the MCTNMCPE were shifted to less positive values with increasing pH. The half-wave potential of the MCTNMCPE at various pH values was calculated as the average value of the anodic and cathodic peak potentials of the CVs. The calculated $E_{1/2}$ values as a function of pH are shown in Fig. 1C. This graph presents a straight line with slope = 52 mV/pH. Such a behavior suggests that it obeys the Nernst Equation for a two-electron and proton transfer reaction.[29]

In addition, the electrochemical behavior of L-Cys (pK_{a1} = 1.92, pK_{a2} = = 8.37, pK_{a3} = 10.7) [30] is dependent on the pH value of the aqueous solution, as well as the MC molecule.

Therefore, pH optimization of the solution seemed necessary for the electro-catalytic oxidation of L-Cys. Thus, the electrochemical behavior of L-Cys in 0.1 M phosphate buffered solutions of different pH values (2.0 < pH < 11.0) at the surface of MCTNMCPE was studied by cyclic voltammetry. It was found that the electrocatalytic oxidation of L-Cys at the surface of MCTNMCPE was more favored under basic conditions than in an acidic environment. This appeared as a gradual growth in the anodic peak current and a simultaneous decrease in the cathodic peak current in the cyclic voltammograms of the MCTNMCPE. The results showed that the maximum peak current can be observed at pH 8. Therefore, pH 8.0 was chosen as the optimum pH for the electrocatalysis of L-Cys oxidation at the surface of the MCTNMCPE.

Electrocatalytic oxidation of L-Cys

The cyclic voltammograms from the electrochemical oxidation of 1.0 mM L-Cys at the MCTNMCPE (curve f), a molybdenum(VI) complex-modified CPE (MCMCPE) (curve e), a TiO$_2$ nanoparticle-modified CPE (TNCPE) (curve d) and the unmodified CPE (curve a) are shown in Fig. 2. As can be seen, the anodic peak potentials for L-Cys oxidation at the MCTNMCPE (curve f) and MCMCPE (curve e) were about 760 mV, while at the TNCPE (curve d), the peak potential was about 835 mV. At the unmodified CPE, the peak potential was about 890 mV (curve b).

From these results, it was concluded that the best electrocatalytic effect for L-Cys oxidation was observed at the MCTNMCPE (curve f). For example, re-

sults show that the peak potential of L-Cys oxidation at the MCTNMCPE (curve f) shifted by about 75 and 130 mV toward negative values when compared with that at the TNCPE (curve d) and unmodified carbon paste electrode (curve b), respectively. Similarly, when comparing the oxidation of L-Cys at the MCMCPE (curve e) and MCTNMCPE (curve f), a dramatic enhancement of the anodic peak current at the MCTNMCPE relative to that obtained at the MCMCPE was observed. In other words, the data clearly show that the combination of TiO_2 nano-particles and mediator (molybdenum(VI) complex) definitely improve the characteristics of L-Cys oxidation. The MCTNMCPE in 0.1 M phosphate buffer (pH 8.0) and without L-Cys in solution, exhibited a well-behaved redox reaction (curve c). Upon addition of 1.0 mM L-Cys. There was a dramatic enhancement of the anodic peak current (curve f), indicating a strong electrocatalytic effect.
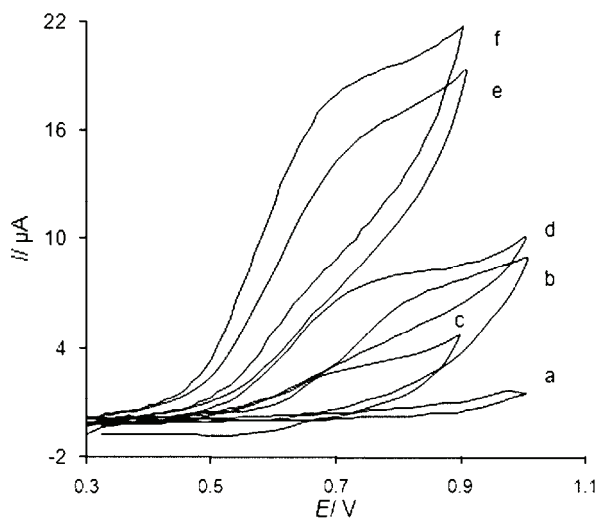
Fig. 2. Cyclic voltammograms of a) CPE in 0.1 M phosphate buffer solution (pH 8.0) at a scan rate 30 mV s^{-1}, b) as a) 1.0 mM L-cysteine, c) as a), d) as b) at the surface of MCTNMCPE and TNCPE, respectively. Also, e) and f) as b) at the surface of MCMCPE and MCTNMCPE, respectively.

Additional information on the rates of these (and other) coupled chemical reactions can be achieved by changing the scan rate (*i.e.*, by adjusting the experimental time scale). In particular, the scan rate controls the time spent between the switching potential and the peak potential.[26] As can be observed from Fig. 3A, the oxidation peak potential shifted with increasing scan rates towards more positive potentials, confirming the kinetic limitation of the electrochemical reaction. In addition, a plot of peak height (I_p) *vs.* $v^{1/2}$, in the range 2–30 mV s^{-1}, was constructed (Fig. 3B). This plot was found to be linear, suggesting that, at sufficient overpotential, the process was diffusion rather than surface controlled. A plot of the sweep rate normalized current ($I_p/v^{1/2}$) *vs.* sweep rate (Fig. 3C) exhibited the characteristic shape typical of an EC process. From the slope of Fig. 3B, the approximate total number of electrons in the overall oxidation of L-Cys

(n) was calculated using the following equation for diffusion-controlled electro-chemically irreversible reactions, in which the first electron transfer is rate-determining:[29]

$$I_p = 2.99 \times 10^5 n((1-\alpha)n_\alpha)^{1/2} A c^* D^{1/2} v^{1/2} \qquad (5)$$

where D is the diffusion coefficient of L-Cys (8.54×10^{-5} cm² s⁻¹, as obtained by chronoamperometry; see later), c^* is the bulk concentration of L-Cys (0.7 mM), and A is the electrode surface area. A value $\alpha = 0.53$ was obtained from the Tafel plots. To obtain information about the rate-determining step, the Tafel plot was drawn (not shown), as derived from points in the Tafel region of the cyclic voltammogram in Fig. 3A. Therefore, an approximate value for the total number of electrons involved in the anodic oxidation of L-Cys, n in the range from 0.7 to ≈1 was obtained.
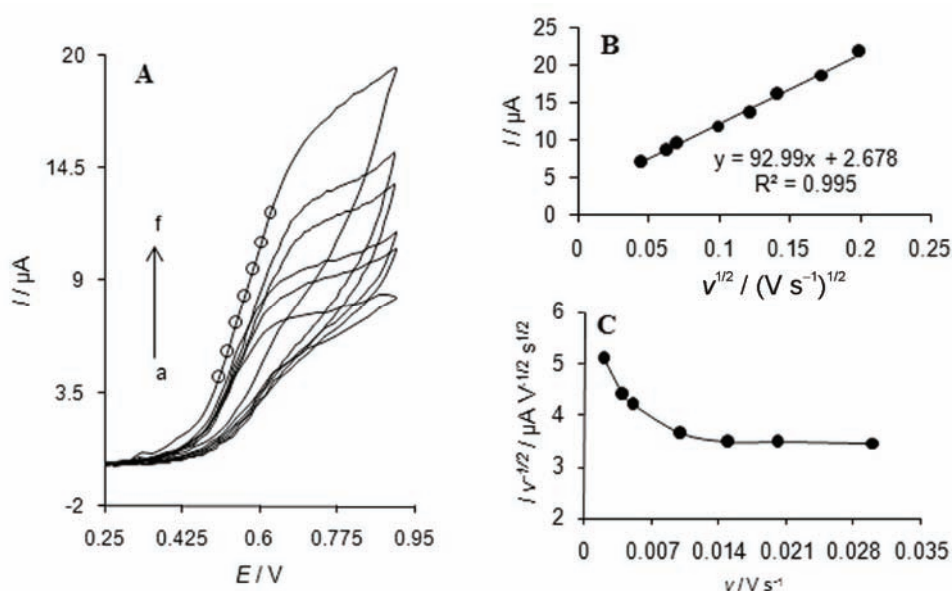

Fig. 3. A) Cyclic voltammograms of the MCTNMCPE in 0.1 M phosphate buffer (pH 8.0) containing 0.7 mM L-cysteine at different scan rates: a) 2, b) 5, c) 10, d) 15, e) 20 and f) 30 mV s⁻¹; B) variation of the electrocatalytic currents *vs.* the square root of scan rate; C) variation of the scan rate-normalized current ($I_p/v^{1/2}$) with scan rate.

Effect of the percent TiO₂ nanoparticles on the behavior of the modified electrode

Figure 4 shows the cyclic voltammograms for 1.0 mM L-Cys in 0.1 M phosphate buffer (pH 8.0) on the surface of molybdenum complex-modified paste electrodes containing various weight percentages of TiO₂ nanoparticles (mixed

with the fine graphite powder to prepare unmodified CPE). As can be seen in Fig. 4, the molybdenum complex-modified electrode without TiO_2 nanoparticles showed a relatively weak and broad wave together with a considerable amount of capacitive current for L-Cys. On the other hand, by addition of 4 mass% of TiO_2 nanoparticles to the graphite powder for preparing the paste, a relatively sharp anodic wave was obtained. The resulting enhancement in the kinetics of L-Cys oxidation together with the remarkable decrease in the capacitive current makes the MCTNMCPE very suitable for the detection of trace amounts of L-Cys in various samples. The maximum sensitivity (anodic peak current) was obtained for the electrode containing 4 mass% TiO_2 nanoparticles, while no enhancement in the current process was obtained with higher amounts. On the contrary, Fig. 4 show that the addition of higher amounts of TiO_2 nanoparticles resulted in lower anodic peak currents. Therefore, in all further electrochemical investigations, 4 mass% TiO_2 nanoparticles was used for preparing the composite pastes.
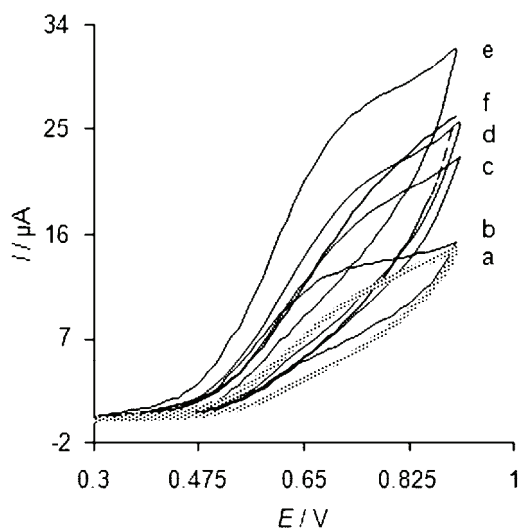

Fig. 4. Cyclic voltammograms of 1.0 mM L-Cys on the surface of a MCMCPE in the absence (a) and presence of TiO_2 nanoparticles in the matrix of the paste: b) 1, c) 2, d) 3, e) 4 and f) 5 mass%.

Chronoamperometric measurements

Chronoamperometry is often used for measuring the diffusion coefficient of electroactive species at the surface area of the working electrode.[26] The chrono-amperometry technique was used to investigate catalytic oxidation of L-Cys by a MCTNMCPE. Chronoamperometric measurements of different concentrations of L-Cys at the MCTNMCPE were realized by setting the working electrode potential at 900 mV. In the chronoamperometric studies, the diffusion coefficient, D, of L-Cys was determined. The experimental plots of I *vs.* $t^{-1/2}$ with the best fits for different concentrations of L-Cys were employed. The slopes of the resulting straight lines were then plotted *vs.* the L-Cys concentration (Fig. 5A), from the

slope of which and using the Cottrell Equation,[29] a diffusion coefficient of $(8.54\pm0.6)\times10^{-5}$ cm^2 s^{-1} was calculated for L-Cys.

The chronoamperometric method of Galus was also used to evaluate the catalytic rate constant, k / M^{-1}s^{-1}, for the reaction between L-Cys and the MCTNMCPE:[31]

$$I_C / I_L = \gamma^{1/2}(\pi^{1/2}\mathrm{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}) \tag{6}$$

where I_C is the catalytic current of L-Cys at the MCTNMCPE, I_L the limited current in the absence of L-Cys and $\gamma = kc^*t$ is the argument of the error function. In the cases where γ exceeds 2, the error function is almost equal to 1 and Eq. (6) can be reduced to:

$$I_C/I_L = \pi^{1/2}\gamma^{1/2} = \pi^{1/2}(kc^*t)^{1/2} \tag{7}$$

where t is the elapsed time. The above equation can be used to calculate the rate constant (k) of the catalytic process. Based on the slope of the I_C/I_L *vs.* $t^{1/2}$ plot (Fig. 5B); k can be obtained for a given L-Cys concentration. Such plots obtained from the chronoamperograms are shown in Fig. 5B. From the values of the slopes, the average value of k was found to be $(6.24\pm0.08)\times10^3$ M^{-1} s^{-1}. The value of k also explains the sharp feature of the catalytic peak observed for the catalytic oxidation of L-Cys at the surface of the MCTNMCPE.
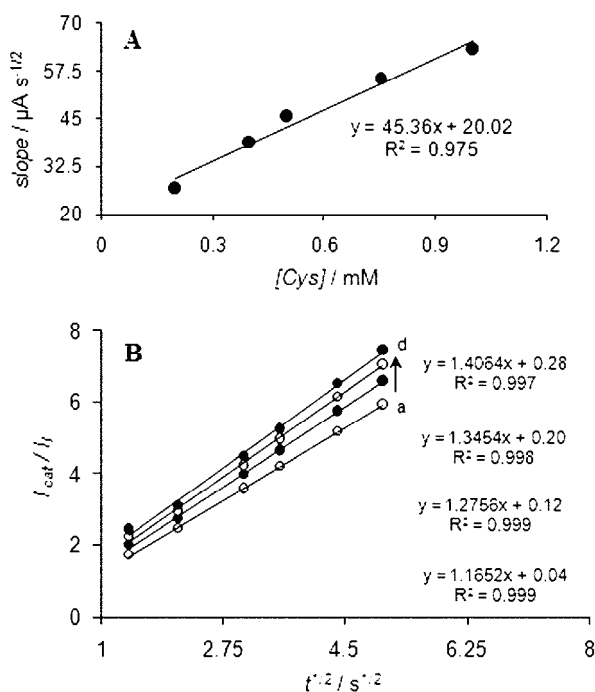

Fig. 5. A) Plot of the slopes of the straight lines against the L-Cys concentration (0.2, 0.4, 0.5, 0.75 and 1.0 mM) obtained from chronoampograms; B) dependence of I_{cat}/I_l on $t^{1/2}$ derived from the data of the chronoamperograms.

Differential pulse voltammetry investigations

Pulse voltammetric techniques are aimed at lowering the detection limits of voltammetric measurements.[26] Since differential pulse voltammetry (DPV) has a much higher current sensitivity and a better resolution than cyclic voltammetry, it was used to estimate the limit of detection of L-Cys. In addition, the contribution of the charging current to the background current, which is a limiting factor in analytical determinations, is negligible in the DPV mode. The responses were linear for L-Cys concentrations in the ranges 1.5–100.0 µM and 100.0–1200.0 µM with current sensitivities of 0.0424 and 0.0082 µA/µM (Fig. 6). The decrease in sensitivity (slope) in the second linear range is probably due to kinetic limitations. From the analysis of this data, the lower limit of detection of L-Cys was estimated to be of the order of 0.70±0.01 µM. This value is comparable to values previously reported by other researchers for the electrocatalytic oxidation of L-Cys at the surface of electrodes chemically modified by other mediators (Table I).[30–33]
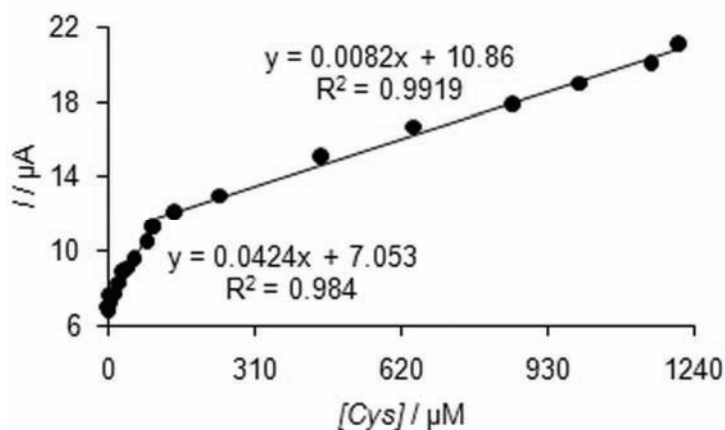

Fig. 6. Plot of the electrocatalytic peak current as a function of L-Cys concentration in the range of 1.5–100.0 µM and 100.0–1200.0 µM obtained from the differential pulse voltammograms.

Interference studies

The influence of various substances, such as $C_2O_4^-$, Br^-, F^-, SO_4^{2-}, NH_4^+, Na^+, EDTA, HPO_4^{2-}, Ca^{2+}, Mg^{2+}, L-cystine, L-phenylalanine, glycine, L-lysine, L-histidine, glucose, SCN^-, L-methionine, L-alanine, L-asparatic acid, L-glutathione, L-tryptophan, tyrosine, ascorbic acid, uric acid and captopril, as compounds that could potentially interfere with the determination of L-Cys under the optimum conditions with 1.0×10^{-5} M L-Cys was studied. The tolerance limit was defined as the maximum concentration of a potential interfering substance that caused an error of less than 5 % for the determination of 1.0×10^{-5} M L-Cys. The

results showed that the peak current of L-Cys was not affected by any of the cations, anions, and organic substances tested.

TABLE I. Comparison of the efficiency of some modified electrodes used in the electrocatalysis of L-Cys

Electrode	Modifier	Method	pH	Peak potential shift, mV	Scan rate mV s^{-1}	Limit of detection M	Dynamic range, M	Ref.
Carbon paste	1-[4-(Ferrocenylethynyl)-phenyl]-1--ethanone	Voltammetry	7.0	350	10	5.0×10^{-6}	2.0×10^{-5}–2.8×10^{-3}	32
Carbon paste	Quinizarine	Voltammetry	7.0	330	50	2.2×10^{-7}	1.0×10^{-6}–1.0×10^{-3}	33
Carbon paste	Ferrocene dicarboxylic acid	Voltammetry	8.0	200	10	1.4×10^{-6}	1.5×10^{-5}–3.2×10^{-3}	34
Carbon paste	Co-complex	Potentiometry	2.4	100	100	5.0×10^{-7}	6×10^{-7}–2×10^{-3}	35
Carbon−TiO$_2$ nano-particle	Molybdenum(VI) complex	Voltammetry	8.0	130	30	7.0×10^{-7}	1.5×10^{-6}–1.2×10^{-3}	This work

Real sample analysis

To evaluate the applicability of the proposed method to real samples, it was applied to the determination of L-Cys in human blood serum, acetylcysteine tablets (purchased from Hexal Company, Germany (specified content of acetylcysteine was 600 mg per tablet) and water samples. The determination of L-Cys in these samples was performed by the standard addition method in order to prevent any matrix effect. Results are presented in Table II. As the tested water samples were found to be free from L-Cys, synthetic samples were prepared by adding known amounts of L-Cys to water samples. The results are given in Table III.

TABLE II. Determination of L-Cys in human blood serum and acetylcysteine tablets (M)

Sample	Human blood serum	Acetylcysteine tablet
Measured value	$(2.17 \pm 0.6) \times 10^{-4}$	$(5.06 \pm 0.5) \times 10^{-3}$
Real value[a]	$(1.48 \pm 4.13) \times 10^{-4}$	5.09×10^{-3}

[a]Result value at 95 % confidence limits, obtained from five replicated determinations per sample

The repeatability and stability of MCTNMCPE

The electrode capability for the generation of a reproducible surface was examined by cyclic voltammetric data (*i.e.*, E_{pa}, E_{pc}, I_{pa} and I_{pc}) obtained in the optimum solution pH from four separately prepared MCTNMCPEs. The calculated *RSD* for various parameters accepted as the criteria for a satisfactory surface

reproducibility was 1–4 %. This is virtually the same as that expected for the renewal of ordinary carbon paste surfaces.[25] In addition, the long term stability of the MCTNMCPE was tested over a four-week period. Cyclic voltammetry of L-Cys at the surface of MCTNMCPE after the modified electrode had been stored under atmospheric conditions at room temperature showed that the oxidation peak potential of L-Cys was unchanged and the anodic peak current decreased by only less than 1.9 % of the initial oxidation peak current. The antifouling properties of modified electrode toward L-Cys and its oxidation product were investigated by recording the cyclic voltammograms of this modified electrode before and after using in the presence of L-Cys. Cyclic voltammetry of L-Cys at the surface of MCTNMCPE after 15 repetition cycles at a scan rate 30 mV s^{-1} showed that the oxidation peak potential of L-Cys remained changed and the anodic peak current decreased by less than 2.9 %. However, in the present study, the surface of the MCTNMCPE was regenerated before each experiment.

TABLE III. Determination of L-Cys in water samples ($n = 5$)

Sample	Added, μM	Found, μM	Recovery, %	*RSD* / %
Tap water	0	–	–	–
	5	4.89	97.8	2.8
	10	9.82	98.2	1.4
	15	15.32	10.2.1	3.2
Well water	0	–	–	–
	5	5.09	101.8	2.9
	10	10.28	102.3	2.1
	15	14.83	98.7	1.3

CONCLUSIONS

In the present study, a carbon-paste electrode modified with TiO$_2$ nanoparticles/bis[bis(salicylidene-1,4-phenylenediamine)molybdenum(VI)] was used for the determination of L-Cys. The CV and DPV investigations showed effective electrocatalytic activity in lowering the anodic overpotential for L-Cys. The high sensitivity and very low detection limit (0.7 μM), together with the ease of preparation and surface regeneration of the modified electrode, and reproducibility of the voltammetric responses are the advantages of the studied modified electrode.

ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ЕЛЕКТРОДЕ МОДИФИКОВАНЕ МОЛИБДЕН(VI) КОМПЛЕКСОМ И TiO₂ НАНОЧЕСТИЦАМА ЗА ЕЛЕКТРОКАТАЛИТИЧКО ОДРЕЂИВАЊЕ L-ЦИСТЕИНА

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Направљен је нов волтаметријски сензор за одређивање L-цистеина (L-Cys) у виду електроде од угљеничне пасте уз додатак TiO₂ наночестица и бис[бис(салицилидин-1,4- -фенилендиамин молибден(VI)] комплекса. Електрохемијско понашање сензора је детаљно испитивано цикличном волтаметријом. Привидна константа брзине преноса електрона и коефицијент прелаза за систем TiO₂ наночестице/комплекс молибдена (VI)/угљенична паста су такође одређени помоћу цикличне волтаметрије и добијене су вредности од око 4,53 s⁻¹ и 0,54, редом. Сензор је показао добру електрокаталитичку активност за оксидацију L-Cys. Потенцијал волтаметријског пика оксидације L-Cys био је за 130 mV нижи у поређењу са истим на немодификованој електроди од угљеничне пасте. Под оптималним условима, линеарна област детекције L-Cys обухвата концентрације од $1{,}5\times10^{-6}$ до $1{,}2\times10^{-3}$ M, док је граница детекције 0,70±0,01 µM при односу сигнала и шума једнаком два. Поред тога, сензор је показао добру стабилност и репродуктивност.

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