



Silica gel modified carbon paste electrode for electrochemical detection of insulin

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ABSTRACT

A silica gel-modified carbon paste electrode (Si-CPE) was fabricated and used for selective and sensitive determination of insulin. The experimental results suggested that insulin effectively accumulated on surface of the modified electrode resulting in a marked enhancement of its oxidation current response. Therefore, the modified electrode was used as an electrochemical sensor for the differential pulse adsorptive stripping voltammetric and hydrodynamic amperometric determination of insulin. The influence of various experimental parameters on the voltammetric response of insulin was investigated. Using hydrodynamic amperometry, under optimum conditions, calibration plot for insulin was linear in the range of 90–1400 pM. The sensitivity and detection limit of the proposed amperometric method were found to be 107.3 pA/pM (1511.3 pA/pM cm²) and 36 pM, respectively. The electrode has the remarkable advantages of simple preparation using inexpensive material, high reproducibility, good chemical and mechanical stabilities, and easy surface renewal owing to bulk modification. The high selectivity of the modified electrode towards oxidation of insulin in the presence of sulfur containing amino acids including cystine, cysteine, and glutathione is a key advantage of the proposed electrode.

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1. Introduction

Insulin is a hormone with extensive effects on both metabolism and several other body functions (e.g. vascular compliance). Insulin causes cells in the liver, muscle, and fat tissues to take up glucose from blood, store it as glycogen, and stop breakdown of fat to be used as an energy source. It serves as a predictor of diabetes of insulinoma and trauma [1,2]. As the level of insulin is a central metabolic control mechanism, its status is also used as a control signal to other body systems such as amino acid uptake by body cells [3]. Therefore, detection of insulin is of great importance for clinical diagnostics. A variety of analytical methods, including immunochemical [4,5], high performance liquid chromatography (HPLC) [6–9], capillary electrophoresis [10,11] and electrochemical methods have been used for determination of insulin [12–22]. However, the use of immunoassays for determination of insulin is complicated by cross reactions and non-specific binding of coexistent bio-molecules in bio-samples to the anti-insulin antibody. On the other hand, the assay systems are insensitive, time consuming and often require multistage steps. Therefore, they cannot be used by clinical laboratories. High-performance liquid chromatography (HPLC) is the method of choice for the analysis of pharmaceutical preparations as well as biological samples. However, this method requires complicated and expensive

instrumentations, professional operators, time-consuming detection process, and complex pre-treatment steps. In recent years, capillary electrophoresis (CE) has become an attractive alternative for the analysis of insulin. Although, this method is known for its high separation efficiency, fast analysis time and simple setup it is not sufficiently sensitive.

The advantages of electroanalytical techniques including high sensitivity, selectivity towards electroactive species, wide linear range, very low detection limit and portable and low cost instruments [23] provide a valuable way for direct determination of trace amounts of various analytes in different samples on a routine basis.

Human insulin is a peptide hormone consisting of a 21-residue A-chain and a 30-residue B-chain, linked by two disulfide bonds. Most amino acids are electroactive, being susceptible to oxidation. However, their oxidation potentials at carbon or bare metal electrodes are too high to be useful for trace determinations [24]. Another serious drawback of the conventional solid electrodes is their fouling during insulin oxidation. These limitations prevent the use of bare solid electrodes as useful electrochemical sensors for insulin determination. In order to overcome these problems and to find a suitable electrochemical insulin sensor, the electrochemical behavior of insulin at various chemically modified electrodes has been studied. The electrochemical oxidation of insulin at a ruthenium oxide/cyanoruthenate (RuO/CN-Ru) modified electrode was studied by Cox and Gray [25]. The proposed electrode is suitable for amperometric determination of insulin in acidic solutions. A multivalent ruthenium oxide (RuO_x) modified electrode which was introduced by Kennedy et al. [26] offered good

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Table 1
Analytical parameters of several modified electrodes for determination of insulin.

Electrode	Method	pH	Dynamic range (nM)	Detection limit (nM)	Sensitivity (nA/ μ M)	Ref.
IrO _x /GC ^a	Amperometry	7.4	50–500	20	35.2	[12]
RuO _x /CPE	FIA ^b	7.4	100–1000	50	0.875	[13]
RuRDMS ^c /carbon electrodes	FIA	7.0	6–400	2	2.3 × 10 ²	[14]
[Ru(bpy)(tpy)Cl]PF ₆ /CCE ^d	Amperometry	7.0	0.5–850	0.4	7.6 × 10 ³	[15]
CNT ^e /GC	FIA	7.4	100–1000	14	48	[16]
Chitosan and CNT/GC	Amperometry	7.4	100–3000	30	1.35 × 10 ²	[17]
K ₄ [Mo(CN) ₈] + Ni/CCE	Amperometry/FIA	7.0	0.5–500 0.10–0.50	0.45 0.04	6.1 × 10 ³ 8.1 × 10 ³	[18]
RuO _x -CNT/carbon electrode	FIA	7.4	10–80	1	5.4 × 10 ²	[19]
Ni nanoparticles/CCE	Amperometry/FIA	13	0.1–700 0.015–0.1	0.040.0026	3 × 10 ⁴ 2.7 × 10 ⁵	[20]
NiO nanoparticles and guanine/GC	Amperometry	7.4	0.1–4000	0.022	10 ⁵	[21]
SiC nanoparticles/GC	FIA	7.4	0.10–0.60	0.0033	10 ⁵	[22]
Ru containing inorganic polymer film/GC	FIA	2.0	1.9 × 10 ⁵ –1.8 × 10 ⁶	–	2.4 × 10 ⁶	[25]
Polynuclear RuO/RuCN/carbon fiber microelectrode	Amperometry	7.4	–	500	0.441	[26]
(RuO _x)/carbon fiber microelectrode	FIA	7.4	100–1000	23	0.072	[27]
Si-CPE	Amperometry	2	0.09–1.44	0.036	10 ⁵	This work
		7.4	0.09–0.63 0.63–1.44	0.052	7.3 × 10 ⁴ 4.2 × 10 ⁴	

^a Glassy carbon.^b Flow injection analysis.^c Ruthenium metallodendrimer multilayers.^d Carbon ceramic electrode.^e Carbon nanotubes.

electrocatalytic effect on the insulin oxidation. However, this electrode was limited by the instability of the RuO_x film at pHs above 5. Gorski et al. performed a systematic study to find a suitable modified electrode for electrocatalytic oxidation of insulin at physiological pHs [27]. A variety of electrocatalysts including polynuclear hexacyanometallates, binary metal oxides, and metallophthalocyanines with various metal centers were tested. The result of their study led to the development of a ruthenium oxide modified electrode with the ability to promote insulin oxidation at physiological pHs. After that, different electrocatalysts including iridium oxide [12], ruthenium metallodendrimer [14], Ru(bpy)(tpy)PF₆ complex [15], carbon nanotubes [16,17], potassium octa-cyano molybdate(IV) [18], nickel nanoparticles [19], ruthenium oxide/carbon nanotube [20], guanine/nickel oxide nanoparticles [21] and silicon carbide nanoparticles [22] were used as electrode modifiers for the electrooxidation of insulin. Most of these modified electrodes offered good analytical performance, as summarized in Table 1, and provided the amperometric detection of insulin at physiological pHs. However, some of these electrodes suffer from poor long-term stability, use of expensive modifiers such as carbon nanotubes, nanoparticles, or require complicated and time consuming methods for preparation of synthetic modifiers. Another drawback which limited the applicability of some of these modified electrodes is lack of surface renewability in case of leaching, contamination or passivation. Therefore, there is still a need for the development of a simple and inexpensive modified electrode for insulin detection with superior long-term stability, simple surface renewability, as well as high sensitivity and precision.

In continuation of our work in the application of silica gel and modified silica gel in the fabrication of chemically modified CPEs [28–35], here we report the use of silica gel in the modification of carbon paste electrode for the amperometric determination of insulin. The electrochemical performance of the modified electrode was investigated and conditions for amperometric determination of insulin were optimized.

2. Experimental

2.1. Instrumentations

A Metrohm electrochemical analyzer model 797 controlled by a microcomputer was used for all voltammetric measurements. Data were acquired and processed (background correction) using 797 VA computrace software 1.2. Amperometric measurements were done by an Autolab PGSTAT 30 Potentiostat Galvanostat (Eco-Chemie, the Netherlands). A three-electrode cell with carbon paste or Si-CPE as working electrode, Ag/AgCl (saturated KCl) as reference electrode and a platinum wire as counter electrode was used.

A Metrohm 827 pH meter was used for pH measurements.

2.2. Chemicals

All chemicals including: silica gel 60 (with mean particle size of 15 μ m), human insulin (27 USP units/mg), amino acids, glutathione, dopamine, ascorbic acids, uric acid, glycolic acid, tartaric acid, glutamic acid, glucose, phosphoric acid, graphite powder, Nujol oil, hydrochloric acid and sodium hydroxide were purchased from Merck and were used as received. All solutions were prepared with deionized water. The stock solution of insulin (70 μ M) was prepared by dissolving insulin in 0.02 M HCl. Insulin solutions were prepared by diluting aliquots of the stock solution with a background electrolyte solution. The phosphate buffer solutions (PBSs) (0.1 M) were prepared from H₃PO₄ and NaOH solutions using the pH meter.

2.3. Fabrication of the modified CPE

The CPE was prepared by adding 0.3 g Nujol oil to 0.7 g graphite powder and thoroughly hand-mixing in a mortar and pestle to produce a homogenous carbon paste. The resulting paste then inserted in the bottom of a Metrohm mini carbon paste electrode (geometrical surface area: 0.71 cm²) and then smoothed on a weighing

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