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Non-enzymatic glucose sensing based on hierarchical platinum micro-/ nanostructures



Tobias Unmüssig^{a,b}, Andreas Weltin^a, Sebastian Urban^a, Patrick Daubinger^c, Gerald A. Urban^{a,d}, Jochen Kieninger^{a,*}

^a Laboratory for Sensors, IMTEK – Department of Microsystems Engineering, University of Freiburg, 79110 Freiburg, Germany

^b Institute of Inorganic and Analytical Chemistry, University of Freiburg, 79104 Freiburg, Germany

^c Johnson Matthey Piezo Products GmbH, 96257 Redwitz, Germany

^d Freiburg Materials Research Center (FMF), University of Freiburg, 79104 Freiburg, Germany

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ABSTRACT

Non-enzymatic glucose monitoring for biomedical applications asks for long-term stable and selective sensors at neutral pH. A hierarchical platinum micro-/nanostructured electrode along with a novel measurement scheme leads to increased sensitivity, selectivity and stability compared to state-of-the-art. The hierarchical electrode coating was applied by a scalable two-step process, which combined electrochemical deposition and colloidal synthesis to obtain a hierarchical structure with high surface roughness. This three-dimensional structure consists of a cauliflower-like platinum deposition, which is coated by a platinum nanowire network. Amperometric glucose measurements showed a 10,000-fold increase in sensitivity $(473 \,\mu A \, cm^{-2} \, m M^{-1})$ compared to unmodified electrodes and linear behavior in the physiological range. The obtained sensitivities are among the highest values reported for non-enzymatic glucose sensors in neutral pH media. The hierarchical morphology provides a selectivity mechanism depending on the reaction kinetics, improving the selectivity for glucose in the presence of the interferent ascorbic acid 2000-fold. Selectivity was further enhanced by low-frequency electrochemical impedance spectroscopy (EIS). Chronoamperometric protocols were developed to achieve long-term stability and overcome the loss of sensitivity due to electrode poisoning. Using chronoamperometric protocols for both the amperometry and the EIS measurements improved stability significantly. The presented results make hierarchical platinum micro-/nanostructured electrodes a promising candidate for continuous glucose monitoring.

1. Introduction

Monitoring of glucose is one of the commercially most important applications for biosensors [1]. The glucose concentration in blood is crucial for patients with diabetes mellitus suffering from too high levels. Currently, mainly enzymatic biosensors are used for the amperometric detection of glucose. The first enzymatic glucose sensor was reported by Clark and Lyons in 1962 using glucose oxidase [2]. The sensing mechanism was based on the measurement of the oxygen consumption due to the enzymatic breakdown of glucose. Since then, enzymatic glucose sensors have been developed extensively [1,3–5]. Still, fundamental disadvantages have not been substantially overcome: The inherent oxygen dependency of the enzymatic oxidation of glucose by glucose oxidase, and the insufficient enzyme stability requiring certain environmental conditions [6]. Therefore, omitting the enzyme would pave the way for an implantable glucose sensor enabling continuous glucose monitoring [7].

In the field of non-enzymatic glucose sensors a lot of research is focusing on different materials as well as electrode structures for the direct oxidation of glucose. Precious metals like platinum or gold are frequently used as electrode material. Especially nanostructured electrodes play a decisive role for the development of sensors with high sensitivity. A variety of different structures were described in literature, such as nanoporous platinum [8–10], platinum nanoflowers [11], gold dendrite-like nanostructures [12] and gold nanowire arrays [13]. Also, non-precious metals like nickel [14] and copper [15] or the more stable oxides NiO [16] and CuO [17] achieve high sensitivities and a low limit of detection. Major drawback of the oxides is the requirement for high alkaline pH, making these materials unsuitable in physiological environments. An overview on the different materials and resulting sensing performance for neutral pH application is provided in Table 1.

For electrode materials in non-enzymatic sensors, achieving a

* Corresponding author at: University of Freiburg, IMTEK – Sensors, Georges-Köhler-Allee 103, 79110 Freiburg, Germany. *E-mail address*: kieninger@imtek.uni-freiburg.de (J. Kieninger).

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Table 1

Comparison of the performances of non-enzymatic glucose sensors in neutral pH media published in literature.

Electrode matrix	Sensitivity in $\mu Acm^{-2}mM^{-1}$	LOD in µM	Linear range in mM	Applied potential	Year and reference
Mesoporous Pt	9.6	-	Up to 10	0.4 V vs. Ag/AgCl	2003 [8]
Nanoporous Pt	291	-	Up to 10	0.4 V vs. Ag/AgCl	2007 [45]
Nanoporous Pt	642	-	0.1–1.5	0.4 V vs. Ag/AgCl	2008 [46]
Nanoporous Pt-Ir	93.7	-	Up to 10	0.1 V vs. Ag/AgCl	2008 [47]
Pt/Te microtubes	522.61	100	0.1-1	0.2 V vs. SCE	2012 [48]
	62.45		1–29		
Nanoporous Pt	10	50	1–10	0.4 V vs. Ag/AgCl	2013 [10]
Pt nanoflowers on graphene oxide	1.26	2	0.002-10.3	0.47 V vs. SCE	2013 [11]
	0.64		10.3–20.3		
AuNP/graphene oxide nanoribbons	59.1	5	0.005-4.92	0.2 V vs. Ag/AgCl	2014 [49]
	31.4		4.92–10		
PtNi/C nanocomposites	1795.1	1	0.002-0.42	-0.05 V vs. SCE	2014 [38]
	707.72		0.5-8.5		
Dendrite Au nanostructures	190.7	50	0.1–25	0.15 V vs. Ag/AgCl	2014 [12]
PtNC/graphene	71.9	30	1–25	0.05 V vs. Ag/AgCl	2015 [39]
Pt-replaced porous Cu	9.62	385	1–11	0.4 V vs. Ag/AgCl	2015 [40]
ZnO nanostructures on MWCNT	64.29	820	1–10	0.12 V	2015 [41]
G-PANI(COOH)-PEI-Fc/Cu-MCNB/GCE	14.3	160	0.5–15	0.53 V vs. Ag/AgCl	2016 [50]
Pt ₃ Ru ₁ nanoparticles	31.3	0.3	Up to 4	0.1 V vs. SCE	2016 [51]
Nanoporous Pt	5.67	800	1–10	0.4 V vs. Ag/AgCl	2017 [52]
Carbon nano-onions	26.5	210	1–10	0.35 V vs. Ag/AgCl	2018 [53]
Pt@ carbon nano-onions	21.6	90	2–28	0.45 V vs. Ag/AgCl	2018 [53]
Hierarchical Pt micro-/nanostructures	473	85	Up to 3	0.45 V vs. Ag/AgCl	This work

sufficient sensitivity at neutral pH, selectivity and stability are major issues, which hinder their commercial application. Typical interfering substances like ascorbic acid, uric acid and 4-acetaminophenol are oxidized in similar potential windows as glucose.

Several strategies to improve selectivity have been proposed: Appropriate selection of catalyst material, electrode structure as well as the oxidation potential. Alternatively, the detection method itself can be improved. The principle of impedimetric detection of glucose using mesoporous platinum electrodes was demonstrated evaluating admittance at a single low frequency [18]. This study compared signals for glucose and ascorbic acid and found higher sensitivity for glucose than ascorbic acid. This was not achieved by amperometry and was explained by the different kinetics of the two reactions.

Long-term stability of non-enzymatic glucose sensors is often limited due to electrode poisoning. In case of platinum, many substances like proteins, or even the reaction products of the direct oxidation of glucose, adsorb on the surface and block catalytic active sites [3,4,19].

In this work, we address selectivity and long-term stability by combining impedimetric detection with chronoamperometric protocols at hierarchical platinum micro-/nanostructures. The electrodes were fabricated by the combination of electrodeposition and colloidal synthesis in a two-step process [20] and showed excellent properties for the direct oxidation of glucose in neutral pH media.

2. Experimental

2.1. Reagents

Dihydrogen hexachloroplatinate(IV) solution (H₂PtCl₆(aq), 33.25 wt % Pt) was purchased from ChemPur Feinchemikalien (Karlsruhe, Germany). Lead(II) acetate trihydrate (Pb(CH₃COO)₂·3H₂O) and formic acid (HCOOH) were obtained from Merck (Darmstadt, Germany). p-(+)-Glucose (C₆H₁₂O₆) and L-ascorbic acid sodium salt (C₆H₇NaO₆) were supplied by Sigma Aldrich (St. Louis, USA). The used electrolytes were 0.1 M PBS (phosphate buffered saline) and 0.5 M H₂SO₄. The PBS composition was 85.2 mM Na₂HPO₄, 14.8 mM NaH₂PO₄ and 0.1 M NaCl. The pH was adjusted to 7.4 by addition of HCl.

2.2. Fabrication of platinum thin-film electrode chips

The thin-film electrode chips were fabricated on borosilicate glass

wafers. Polycrystalline platinum was deposited as thin-film (100 nm) along with titanium adhesion layers by evaporation and covered with a silicon nitride insulation layer. The insulation was opened by reactive ion etching at the position of the electrode (round opening, $200 \,\mu\text{m}$ diameter) and opposite side of the chip to form a contact pad. The detailed fabrication steps of the cleanroom process were described previously [21]. The disk-shaped, polycrystalline platinum thin-film electrodes were used as substrate for the subsequent deposition of the hierarchical platinum micro-/nanostructures.

2.3. Deposition of hierarchical platinum micro-/nanostructures

Hierarchical platinum micro-/nanostructures were obtained by a two-step process. The first step was electrochemical deposition of micro-rough platinum ("platinum black"). The deposition solution was 2 wt% H₂PtCl₆ and 250 mg/l lead(II) acetate in water. Lead acetate was used to improve the deposition especially in case of a high surface roughness following the common recipe [22]. A droplet of 30 µl fresh solution was applied on the electrode. Deposition was done using a programmable current source (Keithley 6221), connected to the platinum thin-film electrode along with a platinum wire as counter electrode. Good adhesion and high surface areas were achieved by deposition with a current ramp, starting from $+4 \text{ mA cm}^{-2}$ to -40 mA cm^{-2} with a slope of 0.061 mA cm}^{-2} s^{-1}. Afterwards, the end current density was kept constant for 30 s.

In the second step the nanostructure was deposited by colloidal synthesis of platinum nanowires at room temperature by a process adapted from literature [23]. For each electrode, 2 ml of the deposition solution were used, which consisted of $2.9 \text{ mM H}_2\text{PtCl}_6$ and 1.26 M HCOOH in water. Deposition time was 7 days in stagnant solution. During this time, the solution turned dark due to formation of platinum particles and larger precipitates. Both before the platinum and before the nanostructure deposition, the electrode surface was pretreated by 10 cycles of cyclic voltammetry in $0.5 \text{ M H}_2\text{SO}_4$ with a scan rate of 100 mV s^{-1} between the potentials for gas formation. Typically, this potential window was between 0 and 1.6 V vs. RHE.

The SEM micrographs in Fig. 1 show the morphology of the hierarchical micro-/nanostructure. The microstructure, deposited by electrochemical deposition, has its characteristic cauliflower-like shape. Higher magnifications reveal the nanostructure formed during the second deposition step, which appears as a fine nanowire network on Download English Version:

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