Sensors and Actuators B 150 (2010) 80–92

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

PtAu/C based bimetallic nanocomposites for non-enzymatic electrochemical glucose detection

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ARTICLE INFO

Article history:
Received 31 May 2010
Received in revised form 14 July 2010
Accepted 24 July 2010
Available online 3 August 2010

Keywords:
Bimetallic nanomaterials
Nanocomposites
Non-enzymatic glucose detection

ABSTRACT

Nanocomposites of Pt:Au (ratios 1:1, 1:2, 1:3 and 1:4) on activated carbon were synthesized using a novel synthetic route, leading to materials with surface enrichment of Pt(0) with high catalytic performance for the direct electro-oxidation of glucose. The overall metallic content (Pt + Au) was 20% (w/w) and the bimetallic nanoparticles were found to be uniformly distributed in the activated carbon (80%) matrix. The surface morphology and composition of the synthesized materials were characterised using scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry was employed in order to confirm the typical metallic electrochemical response of Pt, Au and Pt–Au nanomaterials. The optimum nanocomposite material (Pt_1Au_3/C) for glucose electro-oxidation exhibited a sensitive (4.7 $\mu A\,mM^{-1}\,cm^{-2}$, limit of detection = 2.0 μM) response to glucose over the range 0–10 mM ($r^2 = 0.99$) at $E_{app} = 0.35$ V vs Ag/AgCl under neutral conditions (phosphate buffer solution, pH 7.4). The electrocatalysts showed an excellent response to glucose in comparison to other structurally related sugars (no/negligible response by xylose, maltose, galactose and fructose) and normally co-existing electroactive species (minimal response for ascorbic acid, acetaminophen, uric acid and dopamine). Overall, the materials examined demonstrated excellent glucose sensing capability, while eliminating the pH, temperature sensitivity and lifetime issues associated with enzyme based glucose systems and demonstrate great promise in the quantification of glucose in real clinical samples.

1. Introduction

Diabetes mellitus, a chronic but treatable metabolic disorder, resulting from hyperglycemia and insulin deficiency is reflected by glucose concentrations greater or less than the normal range (4.4–6.6 mM) [1]. Hence, the determination of glucose concentration is extremely important clinically in the diagnosis and treatment of diabetes [2]. Since the first enzyme electrode was reported by Clark and Lyons in 1962 [3], researchers have paid great attention to the development of glucose biosensors and a variety of improvements regarding the immobilization of enzymes and design of redox systems have been reported [4,5].

The application of enzymatic biosensors has been hindered by the inherent fragility of enzymes in addition to complex immobilization procedures which may further decrease the stability of the biocomponent. Glucose oxidase (GOx) is widely used in the fabrication of glucose biosensors and though quite stable compared with other enzymes, is subject to thermal and chemical deformation during fabrication, storage or use. According to Wilson and Turner [6], GOx quickly loses its activity below pH 2 and above pH 8, and temperatures >40 °C can cause fatal damage. The activity of GOx is also very sensitive to the presence of sodium-*n*-dodecyl sulphate at low pH and hexadecyltrimethylammonium bromide at high pH. In addition to temperature, pH and toxic chemicals for sterilisation, glucose sensors are also affected by humidity. Another limitation is the severe interference caused by endogenous electroactive species such as ascorbic acid, acetaminophen and uric acid in blood samples.

A number of studies have been conducted in order to alleviate the drawbacks of enzymatic glucose sensors. Some have focused on retaining and increasing the activity of the enzymes employed, whereas others have focused on the development of non-enzymatic systems [7–10]. Park et al. [11] have reviewed this area recently and many non-enzymatic glucose sensors have been explored, but the selectivity and sensitivity of, for example, Pt

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doi:10.1016/j.snb.2010.07.039

based sensors [9–12] are a critical issue for practical applications. Many of the pure metals (including platinum) exhibit unsatisfactory sensitivity to glucose, are prone to poor selectivity and poisoning by adsorbed intermediates and require alkaline/acidic operating conditions. The aim of recent work, therefore, is to enhance the sensitivity/selectivity towards glucose by investigating more active and lower cost replacements to pure Pt, hence the interest in bimetallic systems. It has been reported that platinum surfaces modified by some heavy metals such as Ir/IrO_2, Pb, Pd and Bi [10,13–16], demonstrated good stability, increased sensitivity and catalytic activity for direct glucose oxidation. However, the dissolution and toxicity of the heavy metal elements are limiting factors in the practical use of such systems.

Interference/selectivity is an important issue for non-enzymatic glucose sensing. This may be addressed by oxidising the glucose electrochemically at remarkably negative potentials [10,14,17] as shown in the case of Pt_2Pb [17], resulting in insensitivity to species such as L-ascorbic acid (AA), uric acid (UA) and acetaminophen (AP). Although Pt_2Pb produces more stable and higher responses relative to pure platinum, surface poisoning by chloride ions remains a critical problem.

Park employed mesoporous structures on the surfaces of pure platinum electrodes [9] and demonstrated good response and sensitivity (9.6 $\mu A\,cm^{-2}\,mM^{-1}$, at 0.4 V) to glucose relative to common interfering species (such as L-ascorbic acid and 4-acetamidophenol) in phosphate buffer solution, even in the presence of high concentration of chloride ions. Selectivity was found to be sufficient for clinical applications while the roughness of nanoscopic dimensions was thought to be responsible for the increased faradaic current of the sluggish reaction. Wang et al. [14] employed nanoporous PtPb electrodes as non-enzymatic glucose sensors which were resistant to chloride poisoning. These electrodes showed sensitive (10.8 $\mu A\,cm^{-2}\,mM^{-1}$) responses to glucose at E_{app} = + 0.4 V in 0.1 M phosphate buffer (pH 7.4) solution and were also capable of sensing glucose at −0.08 V (Ag/AgCl), where the response from the common interfering species (AA, AP, and UA) was effectively avoided. Recently published Pd/SWNTs hybrid nanostructures [10] for the non-enzymatic oxidation of glucose showed high sensitivity (approx. 160 $\mu A\,cm^{-2}\,mM^{-1}$), while common interfering species exhibited minimal response due to the low detection potential (−0.35 V vs SCE).

Continued efforts have been made since the early studies on the electrochemistry of glucose [18–21]. According to Park et al. [11] the α and β forms of glucose may be inter-converted through acid-catalyzed hydrolysis via γ-glucose. The equilibrium ratio of α-, β-, and γ-glucose is 37:63:0.003 under physiological conditions. In both α- and β-glucose, the hydrogen atom tethered to C_1 (dehydrogenation at C_1 carbon) carbon is activated, as the acidity of the hemi-acetalic OH group is stronger than the alcoholic OH. This is well supported by the early studies on electrochemical oxidation of glucose on Pt in neutral phosphate buffer solution [20,22]. β-Glucose is the most reactive species among the possible anomeric forms and the geometric orientation of the hydrogen atom bound to the anomeric carbon is thought to be responsible for the poor reactivity of α-glucose [21]. Mechanistic studies to date have indicated that the overall kinetics of glucose oxidation is too slow to produce significant faradaic current. The final product of the two-electron ($2e^-/2H^+$ process) oxidation of glucose is gluconic acid [11,22], whether glucono-δ-lactone is involved as an intermediate or not.

In order to avoid the current issues associated with non-enzymatic electrocatalysts we have investigated the electrocatalytic activity of carbon supported PtAu based bimetallic nanomaterials. The choice of the Pt–Au pair is based on: (i) the information available in literature [23,24]; (ii) the possibility that Au can show synergism (as in fuel cell reactions) [25–27]; (iii) the fact that synthetic methods can affect the structural characteristics, which contribute to catalytic activity [28] and (iv) the presence of Au can provide stability [29–31], and is promising in minimising the dissolution and toxicity issues associated with heavy metal elements.

The Pt–Au pair is capable of forming homogeneous alloy particles, provided their size is not greater than approximately 3 nm [32], in spite of the fact that in the bulk state there is a wide miscibility gap. Recently, it has been shown that bimetallic nanoparticles are equally important and their catalytic activity depends upon surface properties and optimum utilisation of surface composition [25]. The Pt–Au combination has also proven to be beneficial in so far as it tends to perform better than platinum alone in many applications, e.g., oxygen reduction at a fuel cell cathode [33], alkane isomerisation, when contained in the cages of the HY zeolite structure [34], the selective oxidation of reducing sugars and other polyols [35] and reactions of environmental importance such as nitric oxide reduction by propene [35]. In addition, Adzic and coworkers [30] reported that carbon supported PtAu catalysts exhibited greater stability than carbon supported Pt catalyst for the oxygen-reduction reaction.

Due to the high stability of Au and its co-catalytic or promoting effect, PtAu catalysts have attracted much attention [29]. Sung and coworkers [25] prepared Pt-modified Au nanoparticles using a successive chemical reduction process and investigated its catalytic activity for methanol oxidation. Data indicated that Pt-modified Au nanoparticles exhibited greater catalytic activity for methanol oxidation compared with pure Pt nanoparticles, possibly due to high Pt utilisation in the effective surface structure. Sung and coworkers [26] synthesized PtAu alloy catalysts using the conventional borohydride reduction method and found that this material also showed enhanced activity. However, some researchers suggested an opposite effect of Au, for example, Rojas and coworkers [31] investigated a series of PtAu/C catalysts and found that the role of Au on the methanol oxidation reaction was negligible when alloyed, thus proposing that Au was used as a component of stability. Kumar and Phani [36] prepared unalloyed Pt–Au bimetallic nanoparticles using the polyol method and showed that activity was significantly lowered with increasing content of Au in Pt–Au/C catalyst. These results may be due in part to the different structures and particle sizes of the Pt–Au catalysts obtained. Clearly, it is necessary to explore the appropriate synthetic method to obtain Pt–Au based catalysts with surface structures which can provide optimum utilisation of metallic composition especially for unalloyed catalysts, and to investigate the effect of Au on Pt catalytic activity. Understanding how this combination (alloyed/unalloyed) works requires further exploration in order to reach a definitive conclusion regarding its effect on catalytic activity.

The PtAu/C catalysts presented here demonstrate sensitive and selective amperometric responses to glucose even in the presence of common interfering species such as ascorbic acid (AA), acetaminophen (AP), uric acid (UA) and dopamine (DA) with negligible responses towards structurally related sugars such as maltose, galactose, fructose and xylose over their physiological concentration at neutral pH (7.4). The synergistic role proposed here for Au may be due to its capacity to make Pt more catalytically efficient, by adsorbing or minimising unwanted species/intermediates during the reaction. In addition, there is the possibility of a change in the electronic environment [27,37], which can modify the surface behaviour. The greater electronegativity of Au relative to Pt can cause an increase of the amount of charge transferred from Pt to Au, resulting in an increase in the d-orbital vacancy in Pt–Au, and an alteration in surface behaviour. In general, the magnitude of the depletion of the Au 5d band depends on the fraction of empty states in the valence band of the metal with which it is alloyed [37]. In spite of the fact that electronegativity of Au is higher than Pt, Au