UNIVERSITI TEKNOLOGI MARA

SURFACE PROPERTIES AND ELECTROCHEMICAL PERFORMANCE OF NANOSTRUCTURED GOLD COATINGS ELECTRODEPOSITED ON Au/SPCE FOR GLUCOSE DETECTION

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ABSTRACT

Screen-printed carbon electrode (SPCE) has been extensively employed as a matrix for sensing application. However, the SPCE still has a poor electrochemical activity to be used as a sensing electrode due to its lower conductivity and electrochemical properties than gold. Therefore, in this study, surface modification of SPCE with gold nanostructures coating and their respective electrochemical application as a non-enzymatic sensor for detection of glucose was investigated. Prior to gold nanostructures coating, SPCE was pre-treated by cleaning with H_2SO_4 followed by coating with a gold underlayer (Au/SPCE) to enhance the adhesion of the nanostructured gold coating to the SPCE surface. Two synthesis strategies were used to produce high surface area of gold coatings where first strategy involved the deposition of nanostructured gold using a hydrogen bubbles dynamic template and the second strategy was through dealloying of gold-copper alloy. The deposition parameters such as deposition potentials, deposition time of gold, the molar ratio of alloy electrolytes and also immersion time of the chemical dealloying were optimized to produce gold-based coatings. The modified SPCEs were characterized for their surface morphology, elemental composition, crystallite structures and surface roughness by FESEM, EDX, XRD and AFM, respectively, and their electrochemical and electrocatalytic properties by CV and EIS. The electrochemical performance of the gold electrode for glucose detection was analyzed by CV and CA in 0.1 M NaOH solution. The first deposition strategy produced the optimum gold nanostructures coating, which was deposited at -0.9 V via hydrogen evolution reaction (HER) for 1200 s and labeled as Au-HER (-0.9 V)/Au/SPCE. This gold coating has high electrochemical active surface area (ECSA) (i.e.: 6.337 cm^2) and surface roughness factor of 39.1 with ramified and feather-like branch morphology. The electrochemical kinetic mechanism on its surface was controlled by diffusion. The presence of gold nanostructures on SPCE has significantly enhanced the electrical conductivity and subsequently improved the electron-transfer reaction. Meanwhile, the second strategy using the dealloying process with its alloy composition of 30% gold and 70% copper and labeled as dealloyed Au_{30}:Cu_{70} alloy has shown the highest electrochemical performance as compared to other dealloyed gold electrodes. The dealloyed gold with 98.36 wt.% of gold possesses a three-dimensional network of nested ligaments pores. EDX and XRD measurements confirmed the removal of Cu from the gold alloy. The ECSA value for the dealloyed gold was 6.074 cm^2 with a roughness factor of 37.5. The dealloyed gold coating also gives high electron transfer and low charge-transfer resistance toward Fe $(CN)_6^{-3/-4}$ redox reaction. Among all the synthesized gold electrodes, the Au-HER (-0.9 V)/Au/SPCE electrodes showed the most efficient catalytic role for the non-enzymatic oxidation of glucose sensor with the quickest response (2 s), a low detection limit of 3.16 μM, a wide and valuable linear range (2 mM-9mM), the highest sensitivity (392±4.2 $\mu AmM^{-1}cm^2$) with unmodified for glucose sensor. The Au-HER (-0.9 V)/Au/SPCE electrode was successfully applied for glucose determination in simulated urine samples with good accuracy analysis. These findings contribute to better understanding of the relationship between the deposition parameters used in the synthesis of gold nanostructures electrodes and their surface properties as well as electrocatalytic behaviour for non-enzymatic glucose detection.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nanotechnology has been known field of research since the last century. It generally refers to a field of science and engineering devoted to materials of sizes ranging from 1-100 nm (Herizchi et al., 2016; Mody et al., 2010). Nobel laureate Richard P.Feynman (2016) has reported that various revolutionary developments of nanotechnology with many types of nanoscale levels had been made. The effect of using different size nanomaterials are of the primary goals of nanotechnology to enhance the performance of nanomaterials and to realize the new functionalities that cannot be reached from those observed in fine particles or bulk materials.

Various types of nanosized materials were produced for nanotechnology applications. Nanoparticles are a unique group with a wide class of materials that include broad applications and exceptional features in various fields. Researchers realized that the size of nanoparticles could influence the physicochemical properties of substances. As compared to bulk materials, nanoparticles have improved physical and chemical properties due to their large reactive exposed surface area and quantum size effect as a result of specific electronic structures (Khan et al., 2014).

In recent years, the preparation and potential applications of noble metal gold nanoparticles with diameters between 1 nm and 100 nm have received considerable attention among researchers due to their excellent physical and chemical properties (Liang et al., 2019; Wongkaew et al., 2018). The unique properties of gold nanoparticles are large surface area-to-volume ratio nanostructures, unique optical and electronic properties and convenient surface modification. These properties can improve electrode performance through fast electron-transfer kinetics and decrease overpotentials for electrochemical reactions (Yang et al., 2016). Besides, these favorable properties have brought intensive focus on gold nanoparticles from both research and industry.

Nowadays, advanced synthesis of nanoscale objects can control the design of materials with different shapes, arrangements, sizes and compositions. Consequently, the use of gold nanoparticles or nanostructures in electrochemical biosensors has