



One pot synthesis of poly(5-hydroxyl-1,4-naphthoquinone) stabilized gold nanoparticles using the monomer as the reducing agent for nonenzymatic electrochemical detection of glucose



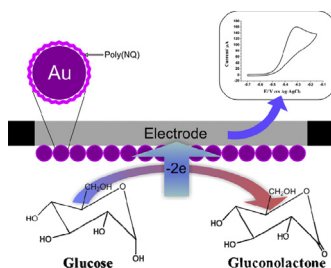
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HIGHLIGHTS

- Polymer stabilized Au nanoparticles were synthesized.
- The monomer was used as the reducing agent.
- The nanoparticle modified electrode is excellent for nonenzymatic detection of glucose.
- Glucose sensing was undertaken under mass transport controlled conditions.
- FTAC voltammetry was employed to obtain mechanistic information.

GRAPHICAL ABSTRACT



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ABSTRACT

Monodispersed and highly stable gold nanoparticles with a diameter between 8 and 9 nm were synthesized in a weakly alkaline medium by chemical reduction of AuCl_4^- using 5-hydroxyl-1,4-naphthoquinone, and stabilized by the simultaneously formed poly(hydroxyl-1,4-naphthoquinone). The electrochemical properties of the resultant poly(hydroxyl-1,4-naphthoquinone) stabilized gold nanoparticles (AuNQ NPs) and its electrocatalytic activity for glucose oxidation in alkaline media were then investigated using a range of techniques, including dc cyclic, rotating disk electrode and Fourier transformed large amplitude ac voltammetry. The results demonstrate that these AuNQ NP modified electrodes exhibit excellent catalytic activity toward glucose oxidation in the potential region where the premonolayer oxidation process occurs. The overall catalytic glucose oxidation process was found to be mass transport controlled under the experimental conditions employed, allowing measurements to be conducted with a high reproducibility. The AuNQ NP modified electrodes showed a high sensitivity of $183 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with a wide linear dynamic range of 0.5–50 mM and a detection limit of 61 μM . However, despite its excellent tolerance toward ascorbic acid, significant interference from uric acid was found with this AuNQ NP modified electrode.

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1. Introduction

Diabetes mellitus is a chronic clinical condition which exhibit high or low deviation in glucose level in blood from the normal range of $80\text{--}120 \text{ mg dL}^{-1}$ (4.4–6.6 mM) [1]. Abnormal levels of glucose cause many long term serious health issues, such as

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blindness, tissue damage, heart disease and kidney failure. Therefore, it is crucial for diabetic patients to regularly monitor the glucose levels with high accuracy. So far, many sensors for glucose monitoring have been reported [2,3]. The majority of these sensors were developed based on the principles of electrochemistry due to the simplicity and low cost of electrochemical sensors [4].

Since direct electrooxidation of glucose is kinetically very sluggish, catalysts are normally required to speed up the process and to offer adequate selectivity that is required for glucose detection in blood samples [5,6]. According to the catalyst used, glucose sensors can be categorized as enzymatic glucose sensors and nonenzymatic glucose sensors [7]. The former class exploit the application of glucose oxidase or glucose dehydrogenase as the biocatalysts [8], while the latter mainly utilize metal nanoparticles (NPs) as the catalysts for glucose oxidation [1,2,5,9]. Enzymes such as glucose oxidase and dehydrogenase, while exhibiting excellent activity and selectivity for glucose oxidation, are unstable in acidic or alkaline media [7,10]. The relatively small active site number to volume ratio is also a drawback in the use of enzymes. In contrast, nanoparticle catalysts are superior in these regards. The state of the art nanotechnology has opened up new opportunities for materials scientists and electrochemists to acquire novel materials which could be employed to replace biocatalysts for electrooxidation of glucose. Particles of gold (Au) and platinum (Pt) metals and alloys have proven attractive for their ability to oxidize glucose with excellent activity [9,11–15]. Interestingly, as the size of the particles goes down the hierarchy, macro to nano, the NPs exhibit more advantageous properties due to the increased percentage of the surface atoms and quantum size effects [16,17].

Polymer stabilized nanoparticle composites have attracted the interest of scientists and have been utilized for the oxidation of glucose in nonenzymatic glucose sensors. Au nanoparticles have received attention for this application due to the ease of synthesis using wet chemical methods with excellent size and shape control [17–19] in addition to their aforementioned high catalytic activity for glucose oxidation. Importantly, the polymer stabilized Au NPs are highly stable, and their high activity is retained due to their relatively weak interaction with the polymer. Consequently, the substrate molecules can easily access the surface of the Au NPs during catalysis. Poyraz et al. prepared poly(*o*-toluidine) (POT) nanofiber/metal nanoparticle composite modified graphite working electrodes which gave rapid responses with a sensitivity of $37 \mu\text{A cm}^{-2} \text{mM}^{-1}$ and a limit of detection (LOD) of $\sim 0.027 \mu\text{M}$ in alkaline medium [7]. Sebez et al. reported the use of polyethyleneimine modified gold nanoparticles on carbon fiber coated with aligned carbon nanotubes in nonenzymatic glucose oxidation at physiological pH of 7.4 [18]. Rong et al. showed that electro-deposited Au nanoparticles coated with polymers with intrinsic microporosity are highly resistive to poisoning during glucose oxidation in pH 7 [20]. Au NPs electrodeposited on amine functionalized mesoporous silica, has been reported to give a sensitivity of $75 \mu\text{A cm}^{-2} \text{mM}^{-1}$ and LOD of $100 \mu\text{M}$ for glucose detection in alkaline medium [12]. Au NPs decorated on multi-walled carbon nanotubes functionalized with congo red composites was reported by Zhou et al. to give a low detection limit of $0.5 \mu\text{M}$ glucose in basic medium [21]. Feng et al. synthesized Au NPs modified with chitosan which was exploited in the application of glucose sensor with a LOD of 0.37mM [22].

In this study, highly stable and monodispersed Au nanoparticles with a diameter between 8 and 9 nm were synthesized conveniently in weak alkaline media using 5-hydroxyl-1,4-naphthoquinone as a reducing agent for AuCl_4^- . The chemical oxidation of 5-hydroxyl-1,4-naphthoquinone by AuCl_4^- leads to the formation of a conducting polymer poly(5-hydroxyl-1,4-naphthoquinone) which in turn stabilizes the Au nanoparticles produced from this

reaction. These poly(5-hydroxyl-1,4-naphthoquinone) stabilized Au nanoparticles (AuNQ NPs) were characterized by a range of electrochemical, spectroscopic and microscopic techniques and their catalytic activity explored for the electrochemical oxidation of glucose in alkaline media.

2. Experimental

2.1. Chemicals

The chemicals 5-hydroxyl-1,4-naphthoquinone (NQ, 97%), gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 99.9%), uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$, 99%), D-(+)-gluconic acid δ -lactone ($\text{C}_6\text{H}_{10}\text{O}_6$, 99.9%) and D-glucose were purchased from Sigma–Aldrich. Sodium hydroxide pellets (NaOH, 99%) were purchased from Merck. The above mentioned chemicals were used as received. Distilled water was utilized for preparation of solutions.

Indium tin oxide (ITO) coated glass slides (surface resistivity: $8\text{--}12 \Omega$ per square, Aldrich) were treated using a literature method, before being used as electrodes [23].

2.2. Preparation of poly(5-hydroxyl-1,4-naphthoquinone) stabilized Au nanoparticles (AuNQ NPs)

To prepare Au NPs, 5-hydroxyl-1,4-naphthoquinone (1.3 mg, $7.5 \mu\text{mol}$) was dissolved in $25.0 \mu\text{L}$ 1 M NaOH ($25 \mu\text{mol}$) aqueous solution and the final volume was made to 5.00 mL with distilled water. The mixture was then stirred using a magnetic stirrer. Upon addition of $50.0 \mu\text{L}$ of 0.1 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ($5.0 \mu\text{mol}$), the solution turned bright purple indicating the formation of Au NPs due to the reduction of AuCl_4^- to metallic Au NPs by 5-hydroxyl-1,4-naphthoquinone and their stabilization by poly(5-hydroxyl-1,4-naphthoquinone) which is simultaneously formed during the reaction via head-to-tail coupling in a manner similar to aniline [24], and presumably provides as a coating layer for the nanoparticles. This solution mixture was stirred for 90 min allowing the reaction to go to completion. AuNQ NPs formed were then isolated using centrifugation at a rotation rate of 8000 rpm (Eppendorf, mini spin plus). Finally the AuNQ NPs were re-dissolved in 1.5 mL distilled water and isolated again using centrifugation to remove impurities. The separated AuNQ NPs were dispersed in 0.5 mL distilled water and stored in a refrigerator for use in subsequent studies. The AuNQ NP dispersion was stable for a long period without any noticeable aggregation of the particles, which implies the excellent stabilizing role of poly(5-hydroxyl-1,4-naphthoquinone).

2.3. Microscopic and spectroscopic characterization of AuNQ NPs

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) measurements were undertaken using a FEI Nova NanoSEM 450 FEG SEM Instrument to determine the surface morphology and the size of AuNQ NPs. EDX analysis was conducted at 10 keV. Images with higher resolution were obtained using a FEI Tecnai G2 T20 TWIN LaB6 transmission electron microscope (TEM). Raman spectroscopic measurements were undertaken using a Renishaw inVia Raman Microscope. An Innova Ar^+ laser (emitting at 514 nm) was used as the light source over the $2000\text{--}400 \text{cm}^{-1}$ range. UV–vis spectra were recorded with a UV–Vis–NIR spectrometer (Cary 5000).

2.4. Fabrication of the AuNQ NPs modified electrode

A glassy carbon electrode (GCE, 3 mm diameter, CH Instruments Inc., Texas, USA) was used to prepare the modified electrode.

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