



Electrochemical deposition of gold nanoparticles-based plasmonic catalyst for glucose oxidation

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Abstract

This work describes an effective electrodeposition method for generating gold plasmonic electrodes which are further used for detecting glucose in solution without the presence of any enzymes (i.e Gox). Under light irradiation, the electro-catalytic oxidation of glucose on the electrodeposited gold nanoparticle (AuNP) surfaces has been investigated. The wavelength-dependent electrochemical oxidative current intensity implies that the hot carriers transferred from the excited plasmonic AuNPs to the absorbed molecules are responsible for enhancing electro-catalysis performance. Hot holes can particularly contribute to the oxidation reaction of glucose on the plasmonic surfaces without the presence of any enzymes in solution. Furthermore, the presence of nano-sized gold particles exhibits a larger active surface area, which leads to a significant improvement in recorded oxidative current for the oxidation of glucose. These results reveal a promising manner for generating non-enzymatic glucose electrochemical sensor upon plasmonic excitation.

Keywords. Plasmonic, gold nanoparticles, electrochemistry, electrochemical catalyst, glucose detection.

1. INTRODUCTION

Recently, noble metal nanoparticles have attracted enormous attention from researchers because of the materials' outstanding optical behavior.^[1-5] Plasmon nanoparticles are well-known as surface catalysis with their strong light absorbance characteristics.^[4,6-7] When the nanoparticles are smaller than the visible wavelength, light can easily penetrate to the whole nanoparticle and grasp at all conduction band electrons.^[8-10] The polarization charges on nanoparticles surface cause the oscillation of free electron clouds. The localized surface plasmon resonance (LSPR) phenomenon happens when photons and free-electrons have matched resonance frequency interact with each other. As a result of LSPR excitation, electron-hole pairs are generated at the surface of nanomaterials.^[11] According to the proposed phenomenon, plasmonic nanoparticles absorb the energy of a suitable frequency in the visible light bandwidth to be activated, hence, those particles can act as an effective photo electro-catalysis in chemical transformation.^[4,7,12-14]

Glucose detection has become an incredibly

crucial issue in clinical analysis, especially for diabetes mellitus patients. Among the different detection devices, glucose oxidase-based biosensors are widely used due to their advantages of high selectivity and good sensitivity.^[15,16] However, the stability and reproducibility characteristics are definitely influenced by the inherent instability of enzyme molecules in the biocomponent.^[17-18] The enzyme is easily lost its catalysis activity and affected by the change in temperature, substrate, and ionic concentration. Moreover, the immobilization procedure of enzymes is complicated and time-consuming process, which requires several steps including storing, activating and recovering enzymes. To overcome those disadvantages of glucose oxidase-based biosensors, non-enzymatic amperometric biosensors for direct determination of glucose is considered as an alternative solution.^[19-20] The outstanding features of non-enzymatic glucose biosensors are stability, simplicity, and reproducibility. Especially, a huge number of studies has focused on non-enzymatic glucose sensors using nanostructures of metal.^[21,22]

Taking advantage of hot holes generated nearby gold nanoparticles (AuNPs) surface upon LSPR excitation.^[23,24] As a consequence, AuNPs may oxidize glucose to produce hydrogen peroxide and gluconic acid, which are the same products as those generated by glucose oxidase (GOx).^[25,26] For that reason, the enzyme can be replaced by plasmonic AuNPs for elaborating the non-enzymatic sensor for glucose detection.^[27-29]

2. MATERIALS AND METHODS

2.1. Chemicals and methods

All chemicals used in this study 0.1 M H₂AuCl₄; phosphate buffered saline PBS pH 7.4, Na₂CO₃, β-D glucose, and NaOH are commercial products. Deionized milliQ water and distilled water were used throughout the experiments.

2.2. Electrochemical deposition of AuNPs on conductive electrodes

All electrochemical experiments were carried out by three-electrode cell Autolab potentiostat/galvanostat instrument (i.e Metrohm). Besides, the Ag/AgCl reference electrode and the Pt counter electrode were utilized. Plasmonic AuNPs were activated by using the laser source of 532 nm.

Both the cyclic voltammetry and multi pulsed chronoamperometry techniques (i.e 5 successive processes for deposition) were used to electrodeposit AuNPs on clean glassy carbon (GC) electrodes. The solution using in those process consists of 0.012 mM [AuCl₄], 0.015 M Na₂CO₃ and PBS 1X.

2.3. Characterization of AuNPs

UV-Visible spectrophotometer was used to evaluate the LSPR of AuNPs over a wavelength varying from 400 to 800 nm. Scanning electron microscopy (SEM) was used to determine AuNPs morphology and sizes.

2.4. Glucose detection

Glucose detections were performed using chronoamperometry method at 0.3 V vs Ag/AgCl with duration of 6000 seconds, in the presence of laser irradiation on electrode surfaces. The system is kept stable for a while before starting to inject 120 μL of 50 mM glucose into the solution for each period of 100 seconds.

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of gold nanoparticles (AuNPs)

Figure 1 shows a cyclic voltammetry curve for depositing AuNPs on GC electrode from an aqueous solution containing 0.5 mM H₂AuCl₄ and 0.25 M Na₂CO₃. In this process, the Ag/AgCl was used as a reference electrode. At the first cycle, non-faradic current was observed at a range potential between 0 to -0.6 V whereas the current significantly increased with the applied potential below -0.6 V. A dramatic increase in the cathodic current was attributed to the change in the double layers between the electrode surface and the solution, due to the gold nucleation process.^[30] At the potential of -0.6 V, the Fermi level of electrode starts to become higher compared to LUMO of Au³⁺, therefore, the electrons from the electrode are able to transfer into the LUMO level of Au³⁺. It is well known as a reduction reaction of Au³⁺ to Au leading the electrochemical deposition of AuNPs on the electrode surface.

In the 2nd cycle, the cathodic current increases clearly at the lower negative potential (i.e. -0.4 V) compared to that observed in the 1st cycle. This proved that the electrode surface has been modified, because of some gold nuclei as well as tiny AuNPs might be deposited on electrode surface after the first scan. It refers to the nucleation process. Moreover, it also reveals that the reduction of Au³⁺ on the as-deposited AuNPs (as seen in the 2nd scan) consumes less energy than the one is carried out on the initial electrode surface (as seen in the first scan). The deposition of gold on the as-deposited AuNPs refers to the growth of AuNPs from its nuclei, so-called growth process.

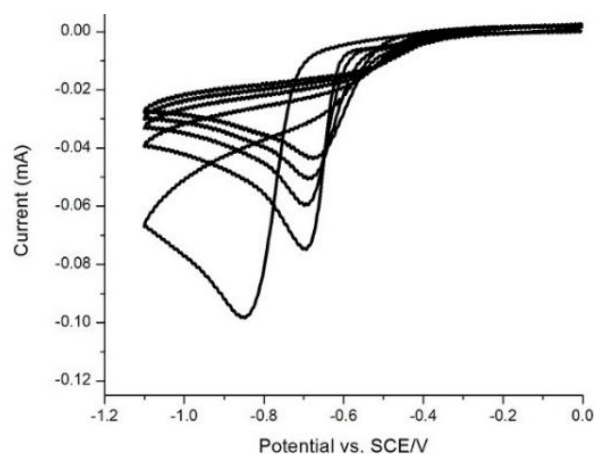


Figure 1: AuNPs deposited on electrode surface by cyclic voltammetry (CVs) technique

To control the AuNPs size, the applied potential

for nucleation and growth process needs to be separated. However, the separation of applied potential during the deposition by the cyclic voltammetry techniques has some challenges. Alternatively, the chronoamperometry technique has been utilized in our previous work^[31] shows a convenient way to separate and well control the applied potential.

In particular, cyclic voltammetry method is applied to determine the potential at which nuclei are created and grown lately. Then, the chronoamperometry technique for the preparation of AuNPs substrates is utilized.

Figure 2 shows the deposition of AuNPs on the electrode by chronoamperometry technique. According to our previous studies,^[30,31] the higher negative potential is applied, the denser nuclei is created. Thus, an applied potential of -1.1 V was chosen for the nucleation process, whereas -0.4 V will be applied for controlling the growth of AuNPs. The succession above is repeated 5 times in order to keep a charge density of 20 mC/cm². It leads to a generation of homogeneous AuNPs on the electrode surface.

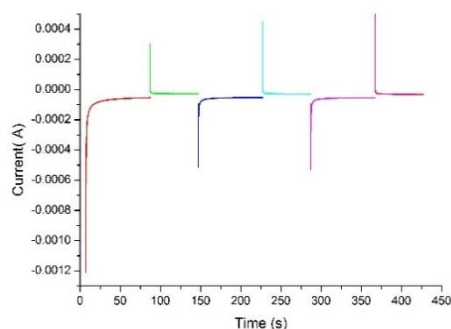


Figure 2: AuNPs deposited on electrode by Chronoamperometry (CA) technique

After the deposition of AuNPs on the electrode surface, the shape, size and density of AuNPs were characterized by scanning electron microscopy (SEM). The SEM image in accordance with the sized analysis graph (figure 3a-3b) shows a random distribution of AuNPs on the electrode surface, which possesses around 50-55 nm diameter spheres.

The modified electrodes are further characterized by UV-Vis spectrometer. Figure 3c shows a strong absorption peak located at 550 nm, which is attributed to the localized surface plasmon resonance (LSPR) of the AuNPs surface. The LSPR phenomenon happens when the interaction of free electrons with photons in light ray causes concerted vibration that is in resonance with the frequency of visible light. When the size of AuNPs is smaller than the exciting light wavelength, the light penetrates the

whole AuNPs and encompasses all the conduction band of AuNPs. As results in the displacement of electrons from their nuclei to form the electron cloud at the one side with respect to the positively charged ions on the other side around nanoparticle named as dipolar. The polarization charges on the particle surface act as a restoring force for the oscillating electrons at a certain frequency. Since these electrons oscillation only occurs nearby the nanoparticle surface, thus it is named as localized phenomena. When the electrode oscillating frequency matched with the excitation frequency of the irradiated light, it reaches to the resonance state and maximizing the oscillating electron magnitudes. This case is called as localized surface plasmon resonance (LSPR).

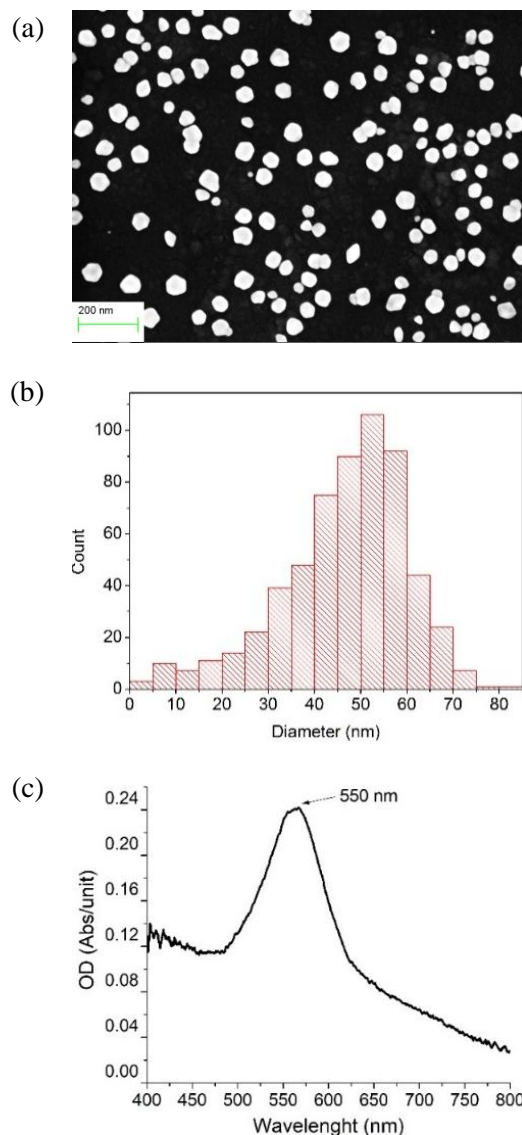


Figure 3: Characterization of AuNPs: (a), SEM image of AuNPs and (b) AuNPs-sized distribution, (c) Optical spectra of AuNPs characterized by UV-Vis spectrometer

3.2. Electrochemical behavior of glucose on various electrodes

In order to elaborate an electrochemical sensor for glucose detection based on plasmonic AuNPs, the electrochemical behavior of glucose on various electrodes (bare glassy carbon (GC) electrode and GC/AuNPs electrode with and without light irradiation) was investigated.

Figure 4 represents differences in glucose electrochemical behavior signal on 3 electrode types. The solid curve depicts the electrochemical response of bare GC electrode in the solution with the presence of glucose. In this case, no Faradic current was observed. It reveals that glucose would not be oxidized on the bared GC surfaces. On the other hand, the dot curve and the dash-dot curve present the behavior of modified electrodes (AuNPs/GC) in glucose solution, with and without light irradiation respectively. Significant anodic current peaks are observed either in case of using ambient light (the dot curve) or using a laser to excite the electrode surface (the dash-dot curve). These anodic peaks might be assigned to the electrocatalytic properties of AuNPs for the oxidation of glucose. It is well-known that the anodic peak current located at 0.3 V vs. Ag/AgCl is attributed to the glucose oxidation peak.^[25]

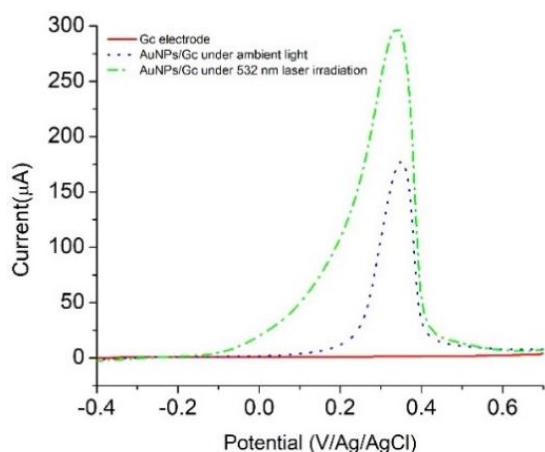


Figure 4: Oxidative current of glucose recorded with using different working electrodes: Gc electrode (a solid curve), AuNPs/Gc under ambient light (a dot curve) and AuNPs/Gc under 532 nm laser irradiation (a dash-dot curve)

Under the irradiation of 532 nm laser, an obvious change in the oxidation peak intensity of glucose is shown in figure 4 (the dash-dot curve). The result clearly explains the influence of laser excitation on the electrocatalytic oxidation of glucose.

3.3. Plasmon-enhanced the electrocatalytic oxidation of glucose in different medium

Using chrono-amperometry methods, a constant potential of 0.3 V vs. Ag/AgCl is applied for the working electrode and records the change in current intensity by the time in the different supporting solutions as shown in figure 5. Basically, biological compounds like glucose are not electroactive molecule.^[26] Consequently, the electrochemical current recorded on bare GC surface with the presence of glucose is at a low current intensity and no signal change in term of the current density neither the laser is on or off (figure 6-a solid curve), this is referred to the insensitive property of glassy carbon surface to glucose.^[26]

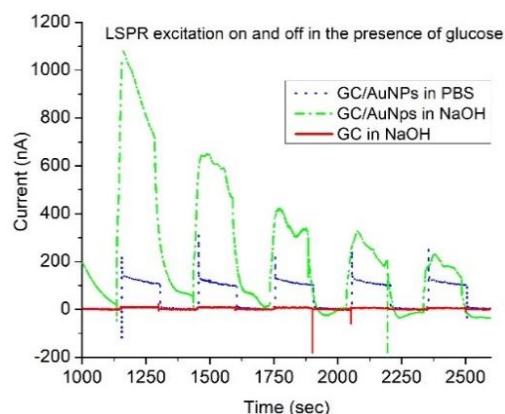


Figure 5: The oxidation behaviors of glucose upon the laser excitation in alkaline supporting solution (a solid curve and a dash-dot curve) and neutral supporting solution (a dot curve)

When AuNPs modified GC electrode creating a plasmonic substrate, which can be used as an active substrate for glucose oxidation. Under the LSPR excitation by 532 nm laser irradiation, the current enhances obviously and disappears immediately when the laser is on and off, respectively (as seen in the dot and the dash-dot curves in figure 5). The differences in recorded current between the on and off state of laser are significant with the highest signal recorded around 1 μ A. However, during the on/off switching experiments, the oxidation reaction of glucose produces gluconic acid near the electrode surface whereas it was easily absorbed causing the decrease of AuNPs's active area. Therefore, a slight decrease of recorded current by the time as illustrated in the dash-dot curve. Moreover, the level of recorded current during laser-off is close to the one recorded on the electrode unmodified with AuNPs (as seen in the solid curve). It proved the electrocatalytic activity of AuNPs toward glucose

oxidation and it implies that LSPR has a strong contribution to the enhancement of electrocatalytic oxidation of glucose on AuNPs surface.

The electrochemical oxidation of glucose is affected by the acidity or alkalinity of the supporting electrolyte solution. Hence, in order to obtain desired signals of electrochemical sensor, the pH impact of the supporting electrolyte solution on the recorded current is also investigated under LSPR excitation.

The significant increase in the electrochemical currents implies the fast transfer of electrons from AuNPs surface to the external circuit, which enhances the recorded signal and makes plasmonic AuNPs as an efficient electrocatalysis in glucose detection. Thus, the higher current peak is, the more electrons are transferred to the external circuit, and this leads to more hot holes are available to assist oxidation process of glucose. Hence, according to the current intensity shown in the dot curve and the dash-dot curve, it clearly demonstrated that the glucose oxidation on gold surface is more effective in alkaline supporting electrolyte solution, compare to the one in neutral medium.

In the alkaline solution, the mass transfer processes are enhanced, due to the fact that the small-sized hydroxyl anions are efficiently diffused into the electrode surface.^[26,32] Consequently, hydroxyl anions from NaOH can be easily oxidized to hydroxyl radical by the high oxidation capacity of hot holes. Being diffused fast into the solution hydroxyl radical oxidized glucose is more efficiently. This way reduces the probability of hot holes and hot electrons recombination to increase the productivity of glucose detection process. As a result, highly alkaline supporting electrolyte solution is more productive than the neutral solution.

3.4. Glucose detection based on plasmonic-electrochemistry catalyst

As-prepared Gc/AuNPs electrodes have been applied to detect glucose in an alkaline solution. The oxidative current of glucose recorded by chronoamperometry technique at 0.3 V with a duration of 750 secs. A certain amount of glucose (ie. 120 μ L glucose 50 mM) has been injected to solution for each period of 100 secs.

Figure 6a shows the current response after each injection of glucose to a solution of 0.1 M NaOH. It is obvious that glucose would not be oxidized on the naked GC electrode, as a consequence of a stable current recorded with the variation of glucose concentration in solution (seen in line 1). When the electrodes are modified by AuNPs, the significant

step-current is observed after each glucose injection, either in case of using ambient light (line 2) or using a laser to excite the electrode surface (line 3). These results are in good agreement with the one presented in figure 4.

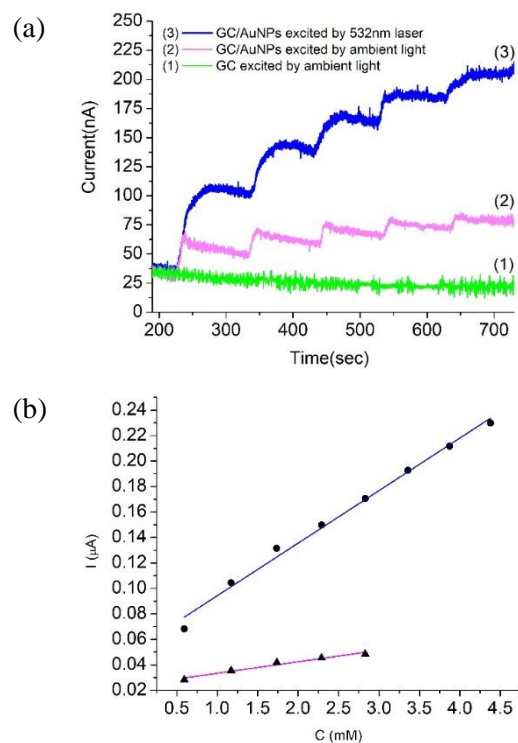


Figure 6: (a) Chronoamperometry glucose detection curves in 0.1 M NaOH on GC electrode (line 1) and on GC/AuNPs without (line 2) and with (line 3) LSPR excitation. (b) Calibration curve of the glucose detection with (a circular symbol line) and without (a triangular symbol line) LSPR excitation

Figure 6b plots the increase in recorded current with the increase in glucose concentration accordingly. The detection sensitivity and limit of detection of glucose performed without the excitation of LSPR (triangular symbol line, figure 6b) is $0.13 \mu\text{Acm}^{-2}\text{mM}^{-1}$ and 0.633 mM , whereas $0.59 \mu\text{Acm}^{-2}\text{mM}^{-1}$ and 0.334 mM with LSPR's excitation (circular symbol line - figure 6b), respectively.

It clearly demonstrated that AuNPs/Gc electrodes excited by laser are more sensitive to glucose oxidation compared to those ones, in which the excitation carried out by ambient light. The obtained results strongly confirm that plasmon enhances electrocatalytic activities of glucose oxidation on AuNPs surface.

4. CONCLUSION

This work reported an effective method for

generating gold plasmonic substrates by using electrodeposition of AuNPs on glassy carbon electrodes. The deposited AuNPs showed a pronounced electro-catalytic activity for glucose oxidation in alkaline solution of NaOH. Moreover, the influences of light irradiation (i.e. ambient light and laser 532 nm) on recorded current intensity demonstrated the LSPR excitation-enhanced electrocatalysis performance. The obtained results provide a promising pathway for upcoming work on the development of non-enzymatic sensor for glucose detection.

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