Nanostructured Gold Microelectrodes for Non-enzymatic Glucose Sensor

Jana Hovancová, Ivana Šišoláková, Petr Vanýsek, Renáta Oriňaková, Ivan Shepa, Marek Vojtko, and Andrej Oriňák

Abstract: A novel, highly stable, selective, and sensitive non-enzymatic glucose sensor was developed by simple and effective modification procedure. The modification of gold microelectrodes by electrochemically deposited gold nanoparticles resulted in increase of surface area up to 37%. The nanostructured surfaces of the gold microelectrodes obtained by different modifications were studied by confocal microscopy, atomic force microscopy, and scanning electron microscopy. The gold nanoclusters exhibit great electrocatalytic properties toward glucose with a wide linear range from 0.5 to 50 mM, with a limit of detection 218 μM, and sensitivity of 185.2 mA mM⁻¹ cm⁻². Moreover, the modified microelectrodes display good reproducibility, stability, and selectivity in the presence of poisoning compounds. Due to the small dimensions of gold microelectrodes and a very small volume of the sample, the microelectrodes make a contribution to miniaturisation of the system.

Keywords: non-enzymatic sensors · miniaturisation · glucose detection · nanostructured gold · gold microelectrodes

1 Introduction

The development of the glucose sensors has attracted significant attention of researchers because of their application in different fields, such as clinical diagnosis, food monitoring, fuel cells and so on [1,2]. Many techniques were applied for glucose detection, such as optical sensors [3,4], electrochemical sensors [5–8], and colorimetry [9]. Among them, electrochemical sensors are widely used due to their high sensitivity, rapid response, low cost, and portability [10]. Up to date, numerous scientific and review papers have been published concerning the glucose sensing, while the majority of articles is focused on clinical detection and the development of an ideal glucose sensor [11–18]. Even though enzymatic sensors are currently widely used in clinical practice and are highly selective due to the specificity of the used enzyme, they display several serious drawbacks. Temperature, humidity, toxic chemicals, and pH could noticeably affect the enzyme activity [9]. Moreover, the instability and the denaturation of the enzyme impacts significantly the fabrication process, storage, and the electrode usage [2]. To overcome these disadvantages of the enzymatic sensors, the scientific community makes an effort to develop a non-enzymatic sensor for glucose detection. The objective is to develop a glucose sensor able to provide glucose oxidation directly on the electrode surface [17]. Recent advances in nanotechnology strongly influenced the development of glucose sensors. Moreover, nanomaterials due to their great catalytic properties originating from their size and shape are able to enhance the kinetics of the glucose oxidation reaction [1]. Nanomaterials provide a higher surface area and variety of surface modification possibilities, which could improve the electron transfer process and could change the value of the reduction potential of a selected metal. Different types of nanomaterials were used for electrode modification, such as nanoparticles, porous particles, nanospheres, nanocages, and nanoboxes [19]. Various material types were applied for glucose sensors development. Among them transition metals [20–22], metal oxides [7,23], bimetallic systems [24–26] or carbon materials [23,26–28] were intensively studied. The transition metals display favourable properties, such as an ability to attain multiple oxidation states. Moreover, transition metals could absorb electroactive species and form intermediates. Application of transition metal nanostructures enhances the mass transport properties, which is important for glucose sensing because of sluggish kinetic of glucose oxidation reaction [29]. Among different transition metal nanomaterials, gold nanostructures are the subject of intense research [30]. The main advantage of gold as a substrate for glucose sensing is the ability to detect glucose in both neutral and alkaline solution. Although the noble metals are more expensive, the transition metals, such as Ni [31], Cu [32], or Co [33] require an alkaline environment because of the catalytic activity of hydroxyl groups. Furthermore, the noble metals display wide linear range,
good sensitivity and more negative potential of glucose oxidation in comparison to other metals. Among them, gold displays lower adsorption of poisoning compounds such as Cl- relative to platinum and nanostructured gold could improve sensing ability in a high concentration of poisoning compounds [15, 17]. The adsorption of poisoning compound depends on pH, with increasing value of pH the adsorption ability decreases [14]. This phenomenon has been ascribed by some authors to repelling effect caused by negatively charged electrode material [34]. Plenty of articles are concerned with electrode material modified by gold nanoparticles (AuNPs) [35–38]. AuNPs are promising candidate for glucose sensing due to its great catalytic properties [39]. The emerging material to load nanoparticles is frequently used to pretend nanoparticles aggregation, but the usage of various material complicate the fabrication process [37]. Direct electrodeposition of gold nanoparticles could overcome complicated preparation and usage of emerging materials [40–42]. For example, Chiang et al. prepared electrodeposition gold nanoparticles surface by studying three different methods of gold surface preparation [43].

In this study, the gold microelectrodes (GME) were used for glucose detection. GME were used because of their small dimensions in comparison with classical three-electrode system or screen printed electrodes. The diameter of the working electrode is only 1 mm and the sample volume is from 3 to 5 μl. These characteristics make a contribution to miniaturisation of the electrochemical system. GME were modified by gold nanostructures, which enlarged the active surface area of the working electrode. Glucose determination was studied in a phosphate buffered saline (PBS) (to simulate the presence of Cl- relative to platinum and nanostructured gold could improve sensing ability in a high concentration of poisoning compounds [15, 17]. The adsorption of poisoning compound depends on pH, with increasing value of pH the adsorption ability decreases [14]. This phenomenon has been ascribed by some authors to repelling effect caused by negatively charged electrode material [34]. Plenty of articles are concerned with electrode material modified by gold nanoparticles (AuNPs) [35–38]. AuNPs are promising candidate for glucose sensing due to its great catalytic properties [39]. The emerging material to load nanoparticles is frequently used to pretend nanoparticles aggregation, but the usage of various material complicate the fabrication process [37]. Direct electrodeposition of gold nanoparticles could overcome complicated preparation and usage of emerging materials [40–42]. For example, Chiang et al. prepared electrodeposition gold nanoparticles surface by studying three different methods of gold surface preparation [43].

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2 Experimental Part

2.1 Chemicals and Reagents

D-(+)-glucose (≥99.5 %), sodium nitrate (≥99 %), hydrochloric acid, Dulbecco’s Phosphate Buffered Saline 10x, K₂[Fe(CN)₆], K₃[Fe(CN)₃]₆, HCl, uric acid, ascorbic acid, and sucrose were purchased from Sigma Aldrich. Sodium hydroxide p.a. was obtained from Milan Adamik, laboratory chemicals, gold(III) chloride (99.9 %) was obtained from Thermo Fisher (Kandel) GmbH. All chemicals were used without further purification. All solutions were prepared with deionized water (18.2 MΩ) and experimental measurements were carried out at room temperature.

2.2 Preparation of the Modified Gold Microelectrode (MGM)

The thin-film gold microelectrodes, purchased from the Micrux Technologies, were used for all electrochemical measurements. Gold microelectrode system consists of three gold electrodes (counter, reference, and working electrode) on a glass substrate covered with an insulating layer (EPON SU8 resin) except for the electrochemical cell (diameter 2 mm-pink circle), as show in Figure 1. The working electrode has a diameter 1 mm. The electrodes were rinsed with distilled water and dried on air prior to modification. Gold microelectrode modification was carried out using cyclic voltammetry method with potential cycling from 0 V to −0.4 V in electrolyte solution consisting of a 0.1 M NaNO₃, 0.25 mM AuCl₃, and 0.25 mM HCl (pH=3) at scan rate 50 mV s⁻¹. The electrochemical deposition of the gold nanostructures was carried out for 4 (GME4Au) and 5 cycles (GME5Au). Electrodeposition was carried out on Solartron Analytical Modulab (mdl. 2100 A). The modified electrode was characterized by scanning electron microscopy (SEM/FIB ZEISS AURIGA), confocal microscopy (PLuneox3D Optical Profiler (SENSOFAR)) and atomic force microscopy (AFM, Dimension Icon by former Veeco Instruments, Inc.-now Bruker).

![Fig. 1. Schematic illustration of the gold microelectrode (RE-reference electrode, WE-working electrode, AE-auxiliary electrode).](image-url)
performed in 0.1 M NaOH and PBS in the potential range from $-1 \text{ V}$ to $1 \text{ V}$. Stability measurements were done in 0.1 M $K_4[Fe(CN)_6]$ and 0.1 M $K_3[Fe(CN)_6]$ as an electrolyte solution and were performed by cyclic voltammetry in the potential range from $-1 \text{ V}$ to $1 \text{ V}$ during 50 cycles. The glucose was diluted into the PBS solution with pH 7.4. Different pH values (1, 3, 11, and 13) were achieved by accurate addition of HCl of NaOH. The solutions with different concentrations of glucose were prepared by dissolving the required amount of glucose in a solution containing PBS and 0.1 M NaOH. Cyclic voltammograms were recorded in the potential range from $-1 \text{ V}$ to $1 \text{ V}$ at scan rate 50 mV s$^{-1}$. Amperometric responses were measured at the potential of 0.46 V for different concentration of glucose in PBS with addition of 0.1 M NaOH.

### 3 Results and Discussion

#### 3.1 Kinetics and Mechanism of Glucose Oxidation Reaction

The cyclic voltammograms (CV) for bare GME were recorded for glucose diluted into the PBS solution. For the optimisation of electrochemical condition, different pHs were studied. As shown in the Figure 2, different pH condition strongly influenced the shape of CV. The CV shows two anodic peaks which probably pertain to glucose adsorption and oxidation in acidic condition (pH 1 and 3). According to difference between the oxidation and reduction potential, the glucose oxidation in acidic condition is irreversible process. The current response is higher in acidic condition in comparison with alkali condition so, it seems to be more suitable for electrochemical determination of glucose. However, during the measurements was the microelectrode surface damaged, which is probably caused be strong Cl$^-$ adsorption. The adsorption of chloride ions in different pH is discussed in the literature [44]. Even if the current response is higher, the electrode is for single use only and the detection is strongly influenced by chloride ions. But in case of alkali condition, the Cl$^-$ adsorption is weaker and so the microelectrode could be used repeatedly. The alkali condition is more suitable, because the electrochemical measurement is less influenced by Cl$^-$ presence and more stable. Moreover, gold microelectrode can be used for much more than one measurement.

The cyclic voltammograms (CV) for bare GME were recorded in PBS with addition of 0.1 M NaOH in the potential range from $-1 \text{ V}$ to $1 \text{ V}$ at 50 mV s$^{-1}$. The CV displays two anodic and two cathodic peaks in the absence of glucose, as shown in Figure 3A.

The anodic peaks in the forward scan can be attributed to the oxidation of Au to AuOH (peak 1., at potential $\sim 0.1 \text{ V}$) and to the oxidation of AuOH to Au$_2$O$_3$ (peak 2., at potential $\sim 0.7 \text{ V}$) [9]. Cathodic peaks (3. at 0.2 V and 4. at $-0.25 \text{ V}$) in the backward scan correspond to the redox processes. The CV for the GME in the presence of glucose is shown in Figure 3B.
10 mM glucose (Figure 3B) has not an obvious shape and the number of anodic peaks increased while the cathodic peaks disappeared in comparison with a CV in the absence of glucose, as shown in Figure 3 B. Three well-defined peaks appeared in the forward scan (peaks I., II., and III.) and one distinct anodic current peak in the backward scan. The peak I. at the potential $\approx 0.1$ V appears in comparison with the CV in the absence of glucose and probably pertains to adsorption of glucose, which is in accordance with the literature [45]. The peaks around the potentials 0.2 V (peak IV.) and 0.4 V (peak II.) can be attributed to glucose oxidation. The peak III. at potential $\approx 0.66$ V corresponds to the peak 2. for CV in absence of glucose. The peaks II. and IV. were studied to achieve the exact mechanism of glucose oxidation. In an effort to study the kinetics and mechanism of glucose oxidation on gold microelectrode, CV were recorded in PBS with addition of 0.1 M NaOH in the potential window from $-1$ V to 1 V at various scan rates (from 5 to 100 mV s$^{-1}$), as shown in Figure 4 A. The peak currents increased with the scan rate. The different linear dependences (Figure 4 B, C, D, and E) were studied to achieve the exact mechanism of glucose oxidation and kinetic parameters. Unfortunately, the peak currents increase linearly with the scan rate ($R^2=0.98$ (peak IV.) and $R^2=0.96$ (peak II.)) as shown in Figure 4 B, but also with the square root of scan rate ($R^2=0.99$ (peak IV.) and $R^2=0.98$ (peak II.)) as shown in Figure 4 C. It follows that, both surface controlled and diffusion controlled processes are possible. However, the linear dependences of log $I$ on log $v$ (Figure 4 D) with linear regression equations log $I=1.0599$ log $v-6.549$, $R^2=0.98$ (peak II.) and log $I=0.1299$ log $v-4.514$, $R^2=0.95$ (peak IV.) indicate that the process is controlled by adsorption and kinetics, respec-
which corresponds to experimental results. By the formation of gold hydroxide, so by the kinetics glucose oxidation again (peak IV.). This process is limited because the gold hydroxide formation involves the adsorbed species desorb from the surface after the electrochemical oxidation. The new surface active sites are forming when the potential is swept to lower values with the formation of gold oxide. As the glucose dehydrogenated glucose molecule is transformed to gluconate by direct oxidation (Eq. 2). The glucose adsorption on the electrode surface. The previous analysis shows, this process is limited by the adsorption of glucose on the electrode surface. The adsorbed species desorb from the surface and with the increasing number of cycles of gold electrodeposition. Also, modified gold electrodes (GME4Au and GME5Au) had uniform and homogeneous surfaces (Figure 5 B1; C1). Instead of the golds, well dispersed and uniform clusters of nanoparticles with diameter of approximately 300–400 nm were deposited. The clusters were formed by spherical gold nanoparticles about 80 nm. The roughness, surface area, and maximum height of the nanostructures layer were measured by AFM (Figure 5A3, B3, C3). All the characteristics of the layer (maximum height, roughness, and surface area) are listed in Table 1. The surface area increase lead to current response increase and enhance also the electrocatalytic activity of glucose sensors. The maximum height of gold nanostructures layer increases with the number of cycles of gold deposition but the surface area do not. This is in consequence of higher amount of nanoclusters on electrode surface caused by the increasing electrodeposition cycles, thereby creating a layer that has reduced surface area. In the case of GME4Au, the maximum height was 410.1 nm and the surface area increased 1.36 times in comparison with the bare electrode (Figure 5 A3). Also, the roughness rapidly increased from 3.74 nm for the bare gold electrode to 62.87 nm for GME4Au. Although the maximum height of the gold nanostructures increased for GME5Au (Figure 5C3), the roughness and the surface area decreased in comparison to GME4Au. The gold clusters grow on the active sites at the microelectrode surface and with the increasing number of cycles of gold deposition the amount of gold clusters increased. In the case of GME4Au, the smaller number of the gold clusters (Figure 5, B4) resulted in the larger surface area (1.088 mm²) in comparison with the GME5Au (1.061 mm²). In the case of GME5Au, the entire surface was covered by the clusters (Figure 5, C4) and as a consequence the surface area was smaller in the final result. In this case, the optimal coverage was achieved by four cycles of electrodeposition even if the maximum height is lower in comparison with GME5Au.

\[
\text{glucose} + \text{OH}^- \rightarrow \text{adsorbed glucose} + \text{H}_2\text{O} + \text{e}^- \quad (1)
\]

\[
\text{adsorbed glucose} + \text{OH}^- \rightarrow \text{gluconate} + \text{H}^+ + \text{e}^- \quad (2)
\]

Based on the Laviron theory, the charge transfer coefficient can be determined using the linear regression equation for the linear dependences of peak potential \(E_p\) on \(\log v\) (Figure 4 E). The number of transferred electrons \(n\) is 2 according to the mechanism of glucose oxidation. The electron transfer coefficient \(\alpha\) was calculated using Laviron’s equation [48]:

\[
E_p = E' + \frac{RT}{(1 - \alpha)nF} \ln \frac{1 - \alpha}{m} \quad (3)
\]

\[
m = \frac{RT k_a}{F \nu} \quad (4)
\]

\[
E_p = left( \frac{E' + \frac{RT}{(1 - \alpha)nF} \ln \frac{1 - \alpha}{m}}{2.303 \log \left( \frac{1 - \alpha}{F \nu} \right)} right) \quad (5)
\]

\[
+ \frac{RT}{(1 - \alpha)nF} 2.303 \log v
\]

\[
slope = \frac{2.303RT}{(1 - \alpha)nF} \quad (6)
\]

\(E_p\) is peak potential, \(E'\) is standard electrode potential, \(k_a\) is rate constant, \(R, T, F\) have an ordinary meaning, \(\nu\) is the scan rate. For the linear regression \(E = 0.237 + 0.0778 \log \nu\), the electron transfer coefficient is 0.62, which is close to 0.5, typical for irreversible processes. The reversibility of the glucose oxidation on gold microelectrodes was unfeasible to determine from the difference between the oxidation and reduction potential because the redox peaks do not occur.

### 3.2 Morphology of Modified Gold Electrodes

The images of the bare GME (Figure 5 A1–4), GME4Au (Figure 5 B1–4) and GME5Au (Figure 5 C1–4) are shown in the Figure 5. The homogeneity of gold microelectrode surfaces was studied by confocal microscopy and SEM as is shown in Figure 5 (A1, B1, C1). The bare GME (Figure 5 A1,2) has the uniform surface with small grains, which could serve as electroactive sites for further gold electrodeposition. Also, modified gold electrodes (GME4Au and GME5Au) had uniform and homogeneous surfaces (Figure 5 B1, C1, C2). Instead of the golds, well dispersed and uniform clusters of nanoparticles with diameter of approximately 300–400 nm were deposited. The clusters were formed by spherical gold nanoparticles about 80 nm. The roughness, surface area, and maximum height of the nanostructures layer were measured by AFM (Figure 5A3, B3, C3). All the characteristics of the layer (maximum height, roughness, and surface area) are listed in Table 1. The surface area increase lead to current response increase and enhance also the electrocatalytic activity of glucose sensors. The maximum height of gold nanostructures layer increases with the number of cycles of gold deposition but the surface area do not. This is in consequence of higher amount of nanoclusters on electrode surface caused by the increasing electrodeposition cycles, thereby creating a layer that has reduced surface area. In the case of GME4Au, the maximum height was 410.1 nm and the surface area increased 1.36 times in comparison with the bare electrode (Figure 5 A3). Also, the roughness rapidly increased from 3.74 nm for the bare gold electrode to 62.87 nm for GME4Au. Although the maximum height of the gold nanostructures increased for GME5Au (Figure 5C3), the roughness and the surface area decreased in comparison to GME4Au. The gold clusters grow on the active sites at the microelectrode surface and with the increasing number of cycles of gold deposition the amount of gold clusters increased. In the case of GME4Au, the smaller number of the gold clusters (Figure 5, B4) resulted in the larger surface area (1.088 mm²) in comparison with the GME5Au (1.061 mm²). In the case of GME5Au, the entire surface was covered by the clusters (Figure 5, C4) and as a consequence the surface area was smaller in the final result. In this case, the optimal coverage was achieved by four cycles of electrodeposition even if the maximum height is lower in comparison with GME5Au.

<table>
<thead>
<tr>
<th>Table 1.</th>
<th>GME</th>
<th>GME4Au</th>
<th>GME5Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum height [nm]</td>
<td>83.7</td>
<td>410.1</td>
<td>597.8</td>
</tr>
<tr>
<td>Roughness [nm]</td>
<td>3.7</td>
<td>62.9</td>
<td>56.1</td>
</tr>
<tr>
<td>Surface area [mm²]</td>
<td>0.797</td>
<td>1.088</td>
<td>1.061</td>
</tr>
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</table>
conditions are an ideal solution in case of gold micro-electrode modification for glucose sensor fabrication.

### 3.3 Electroanalytical Properties

Electroanalytical properties of gold microelectrodes were investigated by cyclic voltammetry measurements in PBS with the addition of 0.1 M NaOH and various concentration of glucose at a scan rate of 50 mV s⁻¹ (Figure 6 A). In an effort to highlight the strong electrocatalytic effect of gold clusters toward the glucose oxidation, cyclic voltammograms for GME, GME4Au, and GME5Au were compared (Figure 6 B). The peak currents increased in the case of modified electrodes in comparison with the bare GME; the highest current response displayed the GME4Au. As was stated in Section 3.2 the surface area for the GME4Au is larger and the roughness is higher, which influences also the current response for the glucose concentration.

![Fig. 5. Confocal microscope images for the bare GME (A1), GME4Au (B1), and GME5Au (C1). SEM images for bare GME (A2), GME4Au (B2), and GME5Au (C2). AFM images for the bare GME (A3,4), GME4Au (B3,4), and GME5Au (C3,4).]
On the basis of the linear dependences of the peak current on glucose concentration (Figure 5C), the modified gold microelectrodes display wide linear range from 500 μM to 50 mM ($R^2 = 0.998$ for GME5Au, $R^2 = 0.99$ for GME4Au). Usually, the requirement for commercialized glucose sensors is from 2 mM to 30 mM, which is the physiological glucose concentration range [14]. So the microelectrodes exceed the lowest and the highest value of the required range. The analytical characteristics (linear range, limit of detection, and sensitivity) for the bare GME, GME4Au and GME5Au are listed in Table 2. The best analytical characteristics displayed the GME4Au with the limit of detection 218 μM and the sensitivity 185.2 μA mM$^{-1}$ cm$^{-2}$. In comparison with the bare GME, the limit of detection decreased 8 times and the sensitivity increased approximately 6 times. The GME5Au showed the 6 times lower limit of detection (351 μM) and 4 times higher sensitivity (106.8 μA mM$^{-1}$ cm$^{-2}$) in comparison with the bare GME. The electroanalytical properties enhancement solely originates from the enlarged surface area of modified electrodes.

The amperometric responses to the addition of different glucose concentration in PBS with addition of 0.1 M NaOH at GME4Au with at an applied potential of 0.46 V are depicted in Figure 7 A. In the Figure 7 B, amperometric response corresponds to the addition of 10 mM glucose in PBS with addition of 0.1 M NaOH. The current response is directly proportional to glucose concentration (according to Cottrel equation) and exhibited linear response from 1 mM to 30 mM ($R^2 = 0.98$) (Figure 7A inset).

The different gold electrode modifications are listed in Table 2 with the aim to compare the electroanalytical properties with the bare and modified gold microelectrodes studied in this work. The gold microelectrodes display the widest linear range in comparison to others already published modified electrodes. Moreover, the linear range is appropriate for glucose detection in real blood samples. Especially, the GME4Au displays the
comparable values of the limit of detection and sensitivity with others electrode modifications.

The gold electrodes suffer from the poisoning compounds absorption, which influences the electrochemical detection of glucose [16]. The gold microelectrodes display good analytical properties in the presence of Cl\(^-\). All measurements were performed in the presence of Cl\(^-\) ions, whose concentration was the same as in biological samples. Also, the PBS was used to simulate the biological condition of the different salts important for human body. Moreover, the modified gold microelectrodes display good selectivity, as shown in Figure 8 A. The CVs were measured for the uric acid (0.5 mM), ascorbic acid (0.1 mM), and sucrose (0.1 mM) in PBS with the addition of 0.1 M NaOH. None of them shows the specific current peak for these compounds, CVs have the same shape and current response as the CV in the absence of glucose. The CV for glucose with addition of interferents displays the same shape as without the presence of the interferent species. In addition, the stability measurement was performed in the 0.1 M K\(_4\)[Fe(CN)\(_6\)] and 0.1 M K\(_3\)[Fe(CN)\(_6\)] solution. The current response increases every of 50 cycles because of charge transfer enhancement and the initial activity for glucose after the 50 cycles was more than 83 %. Long-term stability was also provided. The CV for glucose was measured for the 5 month old modified electrode. The current response for peak which corresponds to glucose oxidation does not decrease and correspond with previous measurements. This corresponds with the favourable properties of gold material. Gold is long-term stable in comparison with other metal materials which are unstable and oxidize. Nine different electrode modifications were used to compare the electroanalytical characteristics of different electrode surfaces with the bare gold electrode, GME4Au, and GME5Au.

### Table 2. Comparison of electroanalytical characteristics of different electrode surfaces with the bare gold electrode, GME4Au, and GME5Au.

<table>
<thead>
<tr>
<th></th>
<th>Linear range [mM]</th>
<th>Limit of detection [µM]</th>
<th>Sensitivity [µA mM(^{-1}) cm(^2)]</th>
<th>References</th>
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<tbody>
<tr>
<td>AuNP/GCE</td>
<td>0.1–25</td>
<td>50</td>
<td>8.5</td>
<td>[49]</td>
</tr>
<tr>
<td>AuNP/ITO</td>
<td>0.001–0.17</td>
<td>0.4</td>
<td>–</td>
<td>[39]</td>
</tr>
<tr>
<td>AuNP film/Si wafer</td>
<td>0.0556–13.89</td>
<td>9</td>
<td>749.2</td>
<td>[50]</td>
</tr>
<tr>
<td>AuHP film/GCE</td>
<td>0.001–0.5,</td>
<td>0.2</td>
<td>–</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>4–12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuNP/PANI/GCE</td>
<td>0.3–10</td>
<td>100</td>
<td>–</td>
<td>[52]</td>
</tr>
<tr>
<td>AuNP/PpyNF/GCE</td>
<td>0.2–13</td>
<td>–</td>
<td>1.003</td>
<td>[53]</td>
</tr>
<tr>
<td>AuNP/Chit/GCE</td>
<td>0.4–10.7</td>
<td>370</td>
<td>–</td>
<td>[1]</td>
</tr>
<tr>
<td>AuNCs/GCE</td>
<td>1–9</td>
<td>100</td>
<td>2131</td>
<td>[19]</td>
</tr>
<tr>
<td>Lamellar ridge Au</td>
<td>0.002–23</td>
<td>0.87</td>
<td>–</td>
<td>[46]</td>
</tr>
<tr>
<td>AuNps/Co(_3)O(_4)</td>
<td>–</td>
<td>0.005</td>
<td>12.5</td>
<td>[7]</td>
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<tr>
<td>Dendride like Au/GCE</td>
<td>0.1–25</td>
<td>50</td>
<td>190.7</td>
<td>[54]</td>
</tr>
<tr>
<td>Bare GME</td>
<td>2–50</td>
<td>1 910</td>
<td>29.5</td>
<td>This work</td>
</tr>
<tr>
<td>GME4Au</td>
<td>0.5–50</td>
<td>218</td>
<td>185.2</td>
<td>This work</td>
</tr>
<tr>
<td>GME5Au</td>
<td>0.5–50</td>
<td>351</td>
<td>106.8</td>
<td>This work</td>
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</table>

Chit-chitosan; GCE-glassy carbon electrode; HP-hierarchical porous; ITO-indium tin oxide glass; NP-nanoparticles; PANI-polyaniline; PpyNF-polypyrrole nanoflowers.

Fig. 7. Amperometric response to the addition of glucose concentration from 1 mM to 30 mM (A), corresponding calibration curve (A inset) and to the addition of 10 mM glucose (B).
electrodes were prepared for reproducibility measurement. The relative standard deviation (RDS) 7.8% was obtained for the current response of modified electrodes.

4 Conclusions

The gold microelectrodes modified by electrochemically deposited gold nanostructures were used for the development of non-enzymatic glucose sensor. The gold nano-clusters exhibited great analytical properties comparable with the already published electrode modifications. The wide linear range from 0.5 to 50 mM overcomes standard with the already published electrode modifications. The gold microelectrodes displayed good selectivity, reproducibility, and stability. Due to small dimensions of gold microelectrodes and a very small volume of sample, the microelectrodes make a contribution to miniaturisation of the system.

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