A SENSITIVE ELECTROCHEMICAL SENSOR BASED ON GOLD NANOPARTICLES DROPLET DEPOSITION ON GLASSY CARBON ELECTRODE FOR BISPHENOL A DETECTION

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ABSTRACT
A convenient, rapid and extremely sensitive electrochemically detection of bisphenol A (BPA) was proposed in phosphate buffer (pH = 7) on a gold nanoparticles modified glassy carbon electrode (GNs/GCE). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were applied for characterization of GNs/GCE. Differential pulse voltammetry (DPV) was employed for measuring BPA. The studies exhibited lower over potentials, improved current response, high reproducibility and lower detection limit at the GNs/GCE versus the bare electrode. Therefore, GNs displays excellent electroactivity toward BPA. Within the concentration range of 1×10⁻⁸ to 6×10⁻⁶M. The fabricated electrochemical sensor demonstrated linear response to BPA with the detection limit of (1.5×10⁻⁹M).

KEYWORDS: Bisphenol A, Gold nanoparticles, Electrochemical sensor, Cyclic voltammetry, Glassy carbon electrode.

INTRODUCTION
BPA is one of the serious industrial waste chemicals. It is known as an environmental endocrine disruptor and carcinogen due to its estrogenic activity (Kinnberg & Toft, 2003; Van Ginkel, Hassan, & Oh, 2010; Yin, Cui, Ai, Fan, & Zhu, 2010). So, BPA has been known as a hazard to human health, because of its undesirable effect on sperm quality and its ability to increase cancer rate. In addition, BPA found to cause diverse pleiotropic actions and reduce immune functions (Steinmetz et al., 1998; L. Zhou, Wang, Li, & Li, 2014). Moreover, it can badly affects wildlife. BPA is widely used in many industrial applications including producing polycarbonate (PC), and epoxy resins. Thus, it is the main component in manufacturing of nursing bottles, food can linings, beverage containers, medical devices for dentistry (Brede, Fjeldal, Skjevrak, & Herikstad, 2003; Kawamura, Sano, & Yamada, 1999; Poorahong et al., 2012). As has been reported, BPA can enter the food from packaging materials and may be eaten by humans (Krishnan, Stathis, Pemnutt, Tokes, & Feldman, 1993; Olea et al., 1996). Therefore developing a sensitive and rapid monitoring to measure the levels of BPA should be considered as our first priority.

So far, various analytical techniques have been tried to detect BPA. These include enzyme-linked immunosorbent assay (ELISA)(Kim et al., 2007; Zhao, Li, Guo, Zhang, & Chang, 2002), liquid chromatography-mass spectrometry (LC-MS) (Sambe, Hoshina, Hosoya, & Haginaka, 2006), gas chromatography-mass spectrometry (GC-MS) (Cunha & Fernandes, 2010; Gatidou, Thomaidis, Stasinakis, & Lekkas, 2007), fluorescence (Molina-Garcia, Fernández-de Córdova, & Ruiz-Medina, 2012) and high pressure liquid chromatography (HPLC) (Wen, Zhou, Xu, Jin, & Feng, 2006). These approaches are very sensitive and selective, they present accurate identification and low limit of detection. On the other hand, they are expensive and time-consuming, they need advanced and complicated instruments and so often there should be operators to use these instruments properly(Chen, Zhang, Cai, Rao, & Long, 2014; Yin, Zhou, et al., 2010; W. Zhou, Sun, Zhou, Yang, & Yang, 2014). Accordingly, nowadays electrochemical sensors are of most interest due to their reliability, low cost, fast response, time saving, simple operation, good selectivity, cheap instruments, real-time and high sensitivity detection compared to other methods.
BPA with the molecular structure as shown in Figure 1 is electrochemically active because of its hydroxyphenyl groups. As a result it can be oxidized at different electrodes (Chauke, Matemadombo, & Nyokong, 2010; Dempsey, Diamond, & Collier, 2004; Portaccio et al., 2010). However fouling effects often causes poor responses at bare electrodes. Thus, in order to overcome this problem, it is essential to modify electrodes by means of materials having electrocatalytic activity, good conductivity and high stability (Raj & Ohsaka, 2001; Shahrokhan, Hamzehloei, Thaghani, & Mousavi, 2004).

In this light our aim is to prepare a desirable electrochemical sensor having high sensitivity and good stability for detection of BPA based on GNs/GC electrode. The peak current of BPA oxidation is significantly heightened at the surface of GNs/GCE in comparison to bare GCE. The CV and DPV results highlighting that gold nanoparticles are efficient sensing materials for determination of BPA.

![Figure 1: Chemical structure of bisphenol A](image)

**MATERIALS AND METHODS**

**Reagents:** BPA was supplied from Sigma Aldrich, K$_2$HPO$_4$ and KH$_2$PO$_4$ were used for preparation of phosphate buffer solution, and HAuCl$_4$ and sodium citrate supplied by Merck. All of the materials were applied without extra purification. The phosphate buffer solution was made of 0.1 M K$_2$HPO$_4$ and 0.1 M KH$_2$PO$_4$ stock solution. Stock solutions of ($1 \times 10^{-2}$M) BPA were prepared by dissolving the chemical in to methanol (HPLC grade) and then stored at 4°C in the dark. All other solutions were provided using deionized water.

**Analysis:** The electrochemical techniques were performed using a potentiostat/galvanostat (IVIUM TECHNOLOGY-VERTEX). A traditional three-electrode system was employed to carry out all electrochemical experiments: Ag/AgCl was utilized as reference electrode. Auxiliary and working electrodes were Pt and glassy carbon, respectively. Field emission scanning electron microscope (FESEM) was performed using a Mira 3-XMU field emission SEM with an acceleration potential of 15 kV.

**Synthesis of gold nanoparticles:** For preparation of colloidal gold nanoparticles as the first step, 100 ml of 0.01% HAuCl$_4$ solution should be heating up to boiling, afterward 2.5 ml solution made by sodium citrate (1%) should be combined with the boiling HAuCl$_4$ and the mixed solution should be maintained at boiling point for 10 minutes, and after that it should be stirred for another 10 minutes in the absence of heat. The resulting solution should be stored at 4°C in dark. By using this method, a 17 nm diameter gold nanoparticles will be obtained.

**Preparation of the BPA electrochemical sensor:** Firstly the surface of bare GCE was mechanically polished with alumina slurry (0.05µm) on a cloth pad and then rinsed ultrasonically in absolute ethanol and double distilled deionized water for a few minutes.

To prepare the modified electrode using a microinjector 5µl of gold nanoparticles was dropped on to the smoothed prepared GCE surface and finally dried at 25°C.

**RESULTS AND DISCUSSION**

**Characterizing of gold nanoparticles:** The morphology of GNs have been investigated by FESEM and the images were operated at 15KV. As can be seen in Figure 2, the synthesized GNs were uniform and spherical in shape with their size ranging from 10 to 25 nm.

![Figure 2: FESEM image of Nano gold on the GC electrode surface](image)
Electrochemical characterization of BPA: According to previous reports (Ntsendwana, Mamba, Sampath, & Arotiba, 2012) the peak current was found to be higher at neutral medium (pH=7). Voltammetric behaviors of $1 \times 10^{-4}$M BPA at bare and GNs modified GCE in phosphate buffer (0.1M, pH=7) were studied using CV and its results were shown in Figure 3. According to the curves, electrochemical behavior of BPA at both electrodes is a quite irreversible reaction. Obviously, in comparison to bare GCE, a considerable enhancement can be observed in the electrochemical response to the oxidation peak current of BPA at GNs/GCE. As is clear, a significant improvement in surface properties of electrode can be seen because of increasing the conductivity of the electrode by gold nanoparticles. Also, it demonstrates the electrocatalytic activity of GNs toward the oxidation of BPA because of the facile electron transfer of GNs and their remarkable conductivity and specific surface area. The bare and GNs/GCE electrode exhibit the oxidation peak current of around 1.099 µA and 1.437 µA around 0.6V for BPA respectively.

![Figure-3: Cyclic voltammograms of $1 \times 10^{-4}$M BPA (a) at bare GCE and (b) $1 \times 10^{-4}$M BPA at GNs/GCE](image)

Electrochemical characterization of GNs/GCE
The investigation of the structure and electrochemical properties of GNs/GCE were carried out using CV and electrochemical impedance spectroscopy (EIS) techniques in potassium ferricyanide as a redox probe (Figure 4).

Figure 4A, displays the cyclic voltammograms of K$_3$Fe(CN)$_6$ at bare and gold nanoparticles modified GCE. The peak current was improved distinctly from 11.75 µA at bare electrode to 6.524 µA at GNs modified GCE. Furthermore, the peak to peak separation ($\Delta E_P$) was obtained as 0.13 for bare GCE and it increased slightly at GNs/GCE. The results show that the GNs can enhance the conductivity and sensitivity of the glassy carbon electrode.

For complementary information about the modified GC electrode, EIS was employed (Figure 4B). The curve a shows the Nyquist diagram of EIS at bare GCE and curve b is the Nyquist plot of GNs/GCE. Electron transfer resistance ($R_{et}$) was found to be 8317 for bare GCE and 6533 for GNs/GCE. Thus the resistance value of the GNs/GCE decreased drastically versus the bare GCE. Accordingly from the EIS, it can be concluded that the GNs modified GCE can efficiently improve the electron transfer rate.
Effect of scan rate: Scan rate effect on electrochemical oxidation behavior of BPA was studied using CV technique in $1 \times 10^{-4}$ M BPA solution (Figure 5A). This method provides further information about the process of BPA oxidation at GNs/GCE. As shown in Figure 5 the peak current of oxidation enhanced proportionally by rising of the scan rate and also, the relationship between scan rate and peak current was linear (Figure 5B). It can be seen that the oxidation of BPA at GNs/GCE is an adsorption-controlled process. In addition, the linear relation was governed between $E_p$ and $\log v$ according to the equation 1, as shown in Figure 5C. The electron transfer coefficient ($\alpha$) was achieved 0.622 by equation 2:

$$E_p = 0.5308 + 0.0392 \log v \quad (1)$$

$$b = 2.303RT/n (1-\alpha) F \quad (2)$$
Where $\alpha$ is transfer coefficient, $n$ is total electrons transferred, $R$, $T$ and $F$ are attributed to gas constant, the absolute temperature and the faraday constant respectively.

**Figure-5:** (A) CVs for BPA ($1\times10^{-3}$M) at GNs/GC electrode in various scan rates (5, 10, 20, 40, 50, 60, 100, 120). (B) Dependency of peak current on the scan rate. (C) The relation between $E_p$ and $\log v$.
Determination of detection limit: Figure 6 displays the DPVs of BPA at the GNS/GC electrode over concentration in the range of $1 \times 10^{-8}$ to $6 \times 10^{-6}$ M. In the mentioned range, the peak current is commensurate with the concentration of BPA and a linear relationship with the correlation coefficient of (0.9874), was obtained for BPA according to the equation:

$$i_p = 6.0086 \mu A \text{ L mol}^{-1} \times [\text{BPA}] + 1.607$$  \hspace{1cm} (3)

Figure 6: (A) Voltammograms of BPA at various concentrations and (B) BPA calibration curve. (In the concentration range of $1 \times 10^{-8}$ to $6 \times 10^{-6}$ M. The BPA lowest limit of detection using this method was attained as low as $(1.5 \times 10^{-9})$ M.)
CONCLUSION
This study proposed not only a convenient but a rapid and authentic electrochemical sensor using GNs/GCE for detecting and measuring BPA. Compared to the bare electrode, at the surface of GNs/GCE an increase in the peak current of oxidation and negative shift of the peak potential of BPA was observed. Due to the high selectivity, low detection limit, wide linear range, reproducibility of the gold nanoparticles modified glassy carbon electrode and the satisfactory results of this method, it could be applied for the determination of Bisphenol A in real sample.

REFERENCES


