One-step electrochemical deposition of Polypyrrole–Chitosan–Iron oxide nanocomposite films for non-enzymatic glucose biosensor

Ali M.A. Abdul Amir AL-Mokaram a,b,*, Rosiyah Yahya a, Mahnaz M. Abdi c,d, Habibun Nabi Muhammad Ekramul Mahmud a,*

a Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
b Department of Chemistry, College of Science, Al-Mustansiriya University, 10052 Baghdad, Iraq
c Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 Serdang, Malaysia
d Institute of Tropical Forestry and Forest Products, University Putra Malaysia, 43400 Serdang, Malaysia

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One-step electrodeposition method of Polypyrrole–Chitosan–Iron oxide (Ppy–CS–Fe3O4) nanocomposite films (Ppy–CS–Fe3O4NP/ITO) has been developed for the fabrication of advanced composite coatings for biosensors applications. The FESEM and EDX results provide the evidence of successful incorporation of Fe3O4 into Ppy–CS molecules. The presence of Fe3O4 nanoparticles in the nanocomposite films was further confirmed by the XRD and XPS spectrums. The fabricated electrode Ppy–CS–Fe3O4 NP/ITO shows a fast amperometric response with high selectivity to detect glucose non-enzymatically with improved linearity (1–16 mM) and the detection limit of (234 μM) at a signal-to-noise ratio (S/N=3.0).

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1. Introduction

In recent years, many researchers have concentrated on the development of glucose biosensors because of their extensive applications in clinical diagnosis [1,2]. The detection of glucose in the blood is the most feasible approach for the measurement of blood sugar concentration [3]. Glucose sensors have already experienced the development of sensors based on enzymatic catalysts and non-enzymatic catalysts. In the past decades, three-generation enzymatic glucose sensors have been developed, but they suffer from the inherent instability of the enzyme due to its pH and temperature sensitivity as well as sensor performance variation due to oxygen concentration variability [4,5]. Additionally, the high cost of enzyme also limits the wide application of enzymatic glucose biosensors in developing countries. Due to the above-mentioned factors, considerable research efforts have been focused on the development of non-enzymatic glucose sensors which allow glucose to be oxidized directly on the electrode surface [6,7].

In order to develop sensitive non-enzymatic glucose sensors, a variety of metals and metal oxides, have been explored [8–11]. Materials such as films or nanocomposite films serve the purpose [12]. Newer approaches focus on developing nanocomposite films. In the bulky polypyrrole (Ppy), electron transfer is relatively slow but coupling with nanostructured materials, the sensitivity is increased due to faster diffusion in the sensing area. The objective of these approaches is to enhance the sensing capabilities of biosensors, such as sensitivity, stability, biocompatibility, reproducibility, and selectivity [13]. Amperometric electrochemical electrodes are receiving widespread attention due to their simplicity, fast response time, and sensitivity to a wide range of biomolecules [14]. These biosensors operate applying a base current between a working electrode and reference electrode, with the reduction or oxidation of a compound causing a shift in the current allowing for quantification of the specific molecules [15]. The nanomaterials in biosensors support the biocompatibility, lifetime, and have been found cost effective [16,17]. Iron oxide (Fe3O4) nanoparticles in composite films have been used for glucose sensors to contribute the electron transfer and increase the surface area of the sensors and thus possess the good electrocatalytic activity [18]. The combination of both metal oxide and the polymeric features throughout the nanocomposite structure lead to great potentials in glucose sensors [19,20].

Herein, we report a novel non-enzymatic glucose sensor produced directly by one-step electrochemical deposition of Ppy–CS–

*Corresponding author at: Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.
E-mail addresses: ali.almokaram@yahoo.com (A.M.A. Abdul Amir AL-Mokaram), ekramul@um.edu.my (H.N. Muhammad Ekramul Mahmud).
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Fe₃O₄ films which have not been addressed before.

2. Experimental

2.1. Preparation of PPy–CS–Fe₃O₄ nanocomposite film

Fe₃O₄ nanoparticles were dispersed into 25 mL of Cs (0.5 mg/mL) solution in acetic acid under continuous stirring at room temperature after which it was sonicated for about 2 h to obtain a viscous solution of CS with uniformly dispersed Fe₃O₄ nanoparticles. Later the solution of pyrrole and (p-TS) (10 mL) was added to the solution of CS and iron oxide and was stirred for 5 min. The prepared solution of Ppy–CS–Fe₃O₄ NP was taken in a glass cell for electrochemical deposition of the film on ITO glass electrode by cyclic voltammetry using three electrode system. The nanocomposite films were then washed repeatedly with distilled water to remove any unbound particles and later dried at room temperature. The detailed mechanism for the deposition is provided in supporting Supplementary information (Section 2.1).

3. Results and discussion

The X-ray diffraction (XRD) patterns of Ppy–CS composite and Ppy–CS–Fe₃O₄ nanocomposite are shown in (Fig. 1a) and (Fig. 1b), respectively. The XRD pattern of Ppy–CS composite film shows a broad peak at \( \Theta \approx 21^{\circ} \) indicating the amorphous form of Ppy–CS composite film (Fig. 1a). However, in Ppy–CS–Fe₃O₄ nanocomposite film, some new sharp peaks at \( 2 \Theta = 21^{\circ}, 29^{\circ}, 34^{\circ}, 37^{\circ}, 45^{\circ}, 50^{\circ} \) and \( 60^{\circ} \) have been observed due to the presence of Fe₃O₄ nanoparticles in the composite films. The XRD pattern of these Ppy–CS–Fe₃O₄ nanocomposite films (Fig. 1b) are polycrystalline in nature [21].

The presence of Fe₃O₄ nanoparticles in the nanocomposite films was further confirmed by X-ray photoelectron spectroscopy (XPS). The XPS wide scan of Ppy–CS composite films and Ppy–CS–Fe₃O₄ nanocomposite films was employed to identify and analyze the chemical components of the films as depicted in (Fig. 1c) and (Fig. 1d), respectively. The major peaks such as C \(_{1\,\text{s}}\), O \(_{1\,\text{s}}\), N \(_{1\,\text{s}}\) were present in the curves for Ppy–CS composite films and Ppy–CS Fe₃O₄ nanocomposite films. New peaks located at the binding energies of 710 eV and 51 eV are assigned to Fe\(_{2\,\text{p}}\) and Fe\(_{3\,\text{p}}\), respectively. In (Fig. 1d), the iron in Ppy–CS–Fe₃O₄ nanocomposite films clearly shows the linkage of Fe₃O₄ nanoparticles onto Ppy–CS composition (Fig. 1c). These peaks of Fe\(_{2\,\text{p}}\) and Fe\(_{3\,\text{p}}\) are for Fe₃O₄ nanoparticles. [22,23].

The glucose sensing performances of Ppy–CS–Fe₃O₄ nanocomposite /ITO and Ppy–CS/ITO electrodes were carefully examined by cyclic voltammetry (CV) in (Fig. 2a) and (Fig. 2b) with and without glucose, respectively. The peak currents for Ppy–CS–Fe₃O₄ nanocomposite /ITO were found to increase dramatically with the addition of 1 mM glucose indicating a good glucose sensing. The peak currents for Ppy–CS/ITO electrode were observed much lower than that of Ppy–CS–Fe₃O₄ nanocomposite /ITO electrode, after adding 1 mM glucose indicating the role of Fe₃O₄ nanoparticle in glucose sensing.

Fig. 3 shows typical steady-state amperometric responses of Ppy–CS–Fe₃O₄ nanocomposite /ITO and Ppy–CS /ITO on...
A sensitivity of 12 into the cell. The results are consistent with those obtained from lower and only show slight increase with the addition of glucose concentrations while the current responses of Ppy shows linearly increased responses to the change of glucose concentration.

**Fig. 2.** (a) CV responses of Ppy–CS–Fe₃O₄ nanocomposite/ITO in 0.1 M NaOH electrolyte with 1 mM glucose and without glucose at the scan rate of 50 mV s⁻¹ (b) CV responses of Ppy–CS/ITO in 0.1 M NaOH electrolyte with 1 mM glucose and without glucose at the scan rate of 50 mV s⁻¹.

**Fig. 3.** Amperometric responses to successive addition of glucose concentration in 0.1 M NaOH solution at +0.18 V (vs. Ag/AgCl). The inset shows the steady-state calibration curve for the of Ppy–CS–Fe₃O₄ nanocomposite/ITO electrode.

successively increasing glucose concentrations at an applied potential of +0.18 V (vs. Ag/AgCl). Ppy–CS–Fe₃O₄ nanocomposite/ITO shows linearly increased responses to the change of glucose concentrations while the current responses of Ppy–CS/ITO were much lower and only show slight increase with the addition of glucose into the cell. The results are consistent with those obtained from cyclic voltammograms. The calibration curve for Ppy–CS–Fe₃O₄ nanocomposite/ITO is presented in the inset of Fig. 3. The glucose sensors show linear dependence in the glucose concentration of dynamic range of 1–16 mM with a correlation coefficient of 0.967, a sensitivity of 12 μA cm⁻² mM⁻¹, and a detection limit of 234 μM (S/N = 3). This novel Ppy–CS–Fe₃O₄ nanocomposite/ITO glucose sensor exhibits high sensitivity, low detection limit and fast response time in less than 3 s.

**4. Conclusions**

In summary, a one-step electrochemical synthesis procedure has been followed to prepare Ppy–CS–Fe₃O₄ nanocomposite films on ITO glass electrode successfully from an aqueous solution containing the monomer, dopant ions, nanoparticles and bio-polymer for glucose sensing. A high glucose sensing performance has been demonstrated by this fabricated sensor with high sensitivity, selectivity, fast response time and low detection limit due to the homogeneous film formation by this one-step electrochemical process. The advantages of low-cost precursor and the simple preparation technique will make the material a promising economical candidate in glucose sensing.

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**Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2016.07.049.

**References**


