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Glucose biosensing applications of polyaniline nanostructures prepared using swollen liquid crystal as 'soft' templates

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ABSTRACT

Nanostructured polyaniline (PANI) was prepared using swollen liquid crystal (SLC) as a soft, structure directing template. Spherical nanoparticles (PANI-0D) and nanorods (PANI-1D) were prepared and the electrocatalytic sensing properties of these nanostructures were compared with bulk-PANI (PANI-B) that was prepared in absence of the template. The cyclic voltametric and chronoamperometric sensitivity of the nanostructured PANI for H_2O_2 detection was better than the sensitivity of the PANI-B. Chronoamperometricsensitivity of the PANI-1D (54.76μA mM^{-1} cm^{-2}) and PANI-0D (35.96 μA mM^{-1} cm^{-2}) was higher than PANI-B (21.92μA mM^{-1} cm^{-2}) in the physiological range of glucose concentration. The PANI-1D nano-sensor showed a low detection limit of 60 μM than PANI-0D (100 μM) and PANI-B (250 μM).The linear range for glucose detection of PANI-1D, PANI-0D and PANI-B were 2-37, 2-28 and 2-28 μM respectively. The PANI-1D nanosensor is insensitive for common interfering agents such as ascorbic acid (AA), uric acid (UA) and dopamine (DA) that are commonly present in human blood.

Keywords:*Nanostructured polyaniline, swollen liquid crystals, glucose sensor, amperometric biosensor.*

1. INTRODUCTION

Development of nanostructures of intrinsically conducting polymers (ICPs) has evolved as an important area of research in the recent years because of their potential applications. PANI is one of the most interesting and widely studied ICPs due to its environmental stability and the tunability of its electrical properties [1]. Nanostructuring of PANI is one of the ways by which properties of PANI can be tuned and enhanced performance can be achieved. Due to the appreciable change in capacitance, optical, electronic and redox properties, when ICPs come in contact with an analyte, they find application in sensing [2]. Development of efficient, sensitive, rapid, cost effective and selective sensors for biological species has received great interest in the recent years from clinical and nonclinical point of view [3]. Glucose is one of the bioanalyte that received much attention because of the prevalence of diabetes in a large proportion of world's population [4]. An efficient and periodic monitoring of blood glucose levels is necessary for diagnosis and management of diabetes mellitus. A number of methods are reported in the literature to synthesize different PANI nanostructures (PANI-NS). We have recently developed a novel method to prepare PANI-NS and its nanocompositesusing swollen liquid crystals (SLCs) as soft templates [5-7]. Morphology of PANI-NS can be modified by tuning the mode of mixing the oxidiser with the aniline containing SLCs [5-7]. Thorough vortex mixing of oxidizer with the aniline containing SLCs led to 0-D nanostructures. Slow diffusion of the oxidizer through the SLCs yielded 1-D nanostructures. The present paper deals with the exploration of H_2O_2 and glucose sensing applications of the PANI-NS synthesized using SLC. The morphology of the PANI-NS strongly influenced the biosensing.

2. EXPERIMENTAL SECTION

Bulk-PANI (PANI-B) was synthesized using already reported procedure [8]. Two PANI-NS of different morphology, one having spherical morphology (PANI-0D) and another having rod shape (PANI-1D), both having 10 % aniline were synthesized using our previously reported method [5]. Thorough characterization of the same using different techniques such as UV-Visible, FTIR, XRD, FESEM and AFM were already reported [5]. The PANI samples were deposited on gold printed PCB strips having three electrode configuration using conventional screen printing technique for the electrochemical studies. Ethyl Cellulose (EC) was used as temporary binder and Butyl Carbitol Acetate (BCA) as diluent. The optimum composition of the ink was EC (10 mg), BCA (75 μl) and PANI (10 mg). Typically, ~0.5 mg of PANI gets printed on the PCB strips. Gluteraledyhe was used as a crosslinking agent for immobilizing the glucose oxidase (GOx) enzyme while making the biosensor. 5 μl of 1% gluteraldehyde in PBS buffer (pH=7.2) was placed on the sample area of the electrode and then the electrode was placed in a humid chamber for 4 h followed by rinsing with 0.1 M Phosphate buffer (pH=7.2). Then 10 μl of GOx (10 mg/ml in PBS buffer) was placed on the gluteraldehyde treated sample area of the electrode. The electrode was then placed in a humid chamber for the next 24 h before performing sensing studies. CV and chronoampometry were used for testing the electrochemical sensing of H_2O_2 and glucose. Continuous amperometric studies were done in phosphate buffer (pH=7.2) by applying potential of 0.4 V with successive addition of 100 μl of H_2O_2 solution.

3. RESULTS AND DISCUSSION SECTION

For H_2O_2 sensing, CV studies were done with different concentration of H_2O_2 in phosphate buffer (pH=7.2) as shown in Fig. 1. It was found that PANI-1D (Fig. 1a) showed higher peak current values than PANI-0D (Fig. 1b) and PANI-B (Fig. 1c) for the same concentration of H_2O_2. Hence, PANI-1D has very high voltametric sensitivity for H_2O_2 than PANI-0D and PANI-B. The amperometric responses for the three PANI samples for sequential addition of small volumes of H_2O_2 are shown in Fig. 2a. The potentiostat was kept paused while adding each aliquot to avoid recording the noise during mixing. Hence, accurate estimate of response time could not be measured. Nevertheless the addition of aliquots and mixing was completed in less than 10 s and hence the response time is less than 10 s for all the samples. PANI-1D showed highest sensitivity to H_2O_2 (46.97 µA mM^{-1} cm^{-2}) followed by PANI-0D (3.8 µA mM^{-1} cm^{-2}), while PANI-B showed the least sensitivity (2.4 µA mM^{-1} cm^{-2}). The calibration plot between concentration of H_2O_2 and current values were plotted and are shown in Fig. 2b. All the samples showed linear dependence for variation of current with concentration of H_2O_2 in the tested range (2 mM to 28mM). Detection limit for PANI-1D, PANI-0D and PANI-B was 40, 60, and 100 µM respectively at a signal to noise ratio of 3.

After having established the high sensitivity of PANI-1D for the H_2O_2 sensing, we tested the amperometric glucose sensing activities of PANI samples in presence of GOx by applying potential of 0.4 V. The amperometric response for successive addition of 100 µl glucose solution was recorded in the physiological range of glucose in human blood and the results are shown in Fig. 3 a. There was sudden rise in the amperometric current on each addition of small volumes of glucose solution and a plateau was achieved in less than 10 s. PANI-1Dshowed linear response in currentas 2-37 mM, PANI-0D (2-28mM) and PANI-B (2-28mM) to successive addition of glucose concentration in the calibration curves shown in Fig. 3b. This covers the complete physiological range of glucose concentration. Sensitivity of the PANI-1D (54.76 µA mM^{-1} cm^{-2}) was higher than PANI-B (21.92 µA mM^{-1} cm^{-2}). PANI-0D (35.96 µA mM^{-1} cm^{-2}) also showed better sensitivity than PANI-B. The detection limit for PANI-1D, PANI-0D and PANI-B were 60 µM, 100 µM and 250 µM respectively at a signal to noise ratio of 3.

Biosensor for physiological glucose detection should not only be sensitive, but also be highly selective. We tested amperometric response for the addition of 1 mM each of ascorbic acid (AA), uric acid (UA), dopamine (DA) and glucose using PANI-1D as sensing material as shown in Fig. 4. AA, UA and DA are generally present along with glucose in human blood. PANI-1D was almost insensitive to AA, UA and DA while showing high sensitivity for glucose. Insensitivity to AA, UA and DA can be due to the low potential (0.4 V) that we used in our studies. Higher sensitivity exhibited by PANI-1D over PANI-0D and PANI-B for both H_2O_2 and glucose is mainly due to the higher surface area and improved crystallinity of the former. The higher sensitivity of nanostructured-PANI must be arising out of its increased surface area that facilitates the intimate contact between the analyte and the active material.

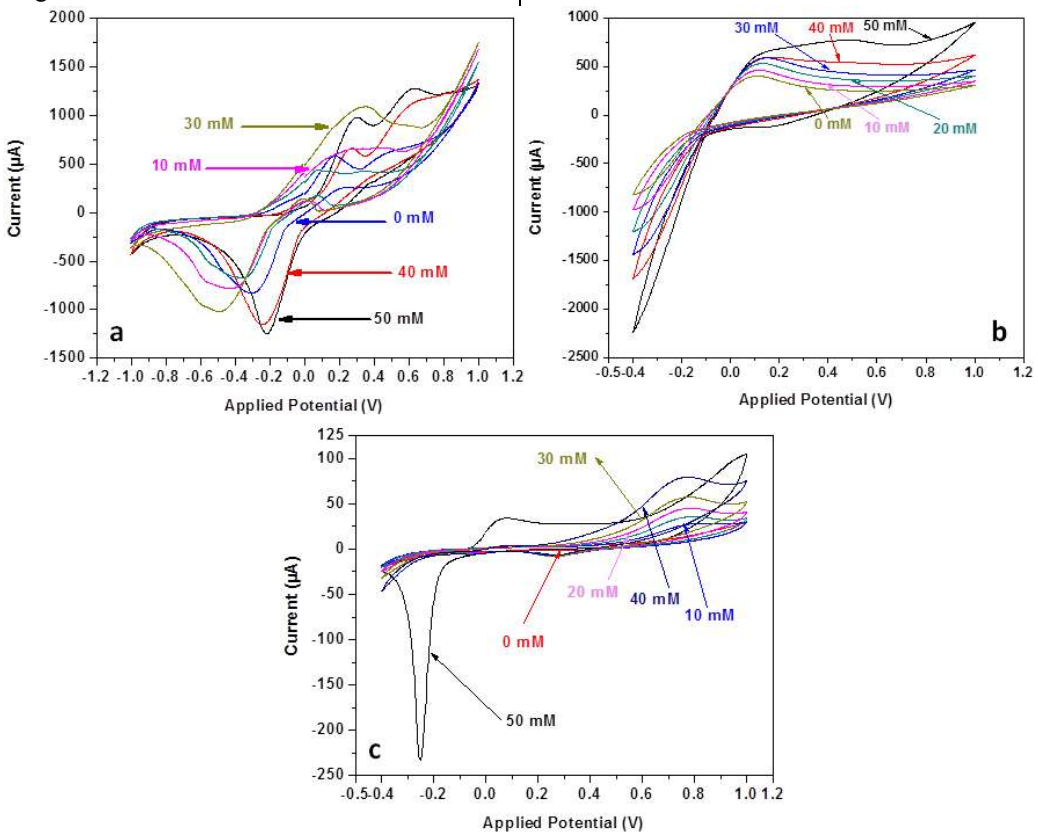

Figure 1. (a) CV of PANI-1D nanostructures; **(b)**PANI-0D nanostructures and **(c)**PANI-B in PBS buffer (pH=7.2) with different concentration of H_2O_2.

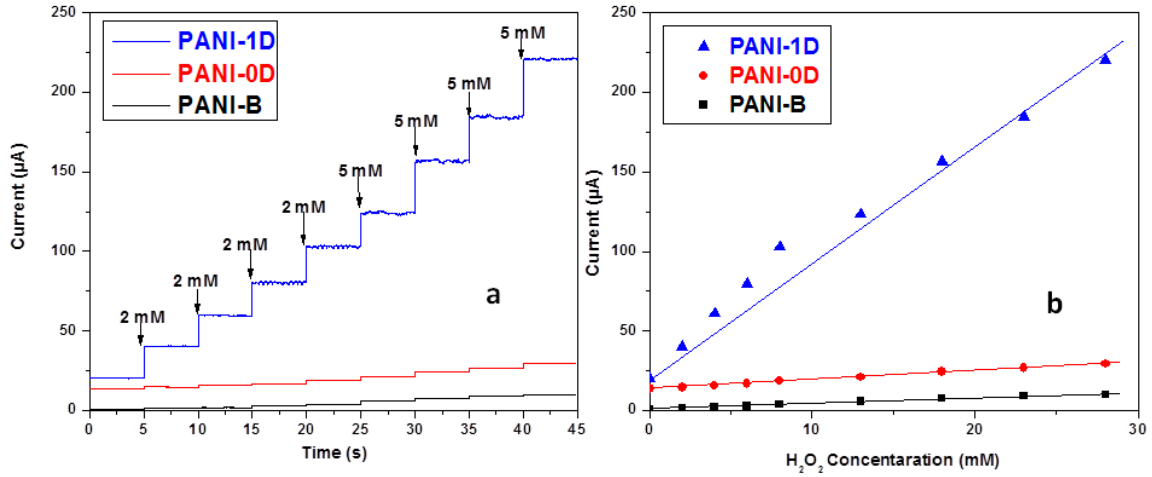

Figure 2. (a) Chronoamperometric response of PANI-1D, PANI-0Dnanostructures and PANI-B for change in concentration of H_2O_2 in PBS buffer (pH=7.2). **(b)** Calibration curves corresponding to the chronoamperometric H_2O_2 detection.

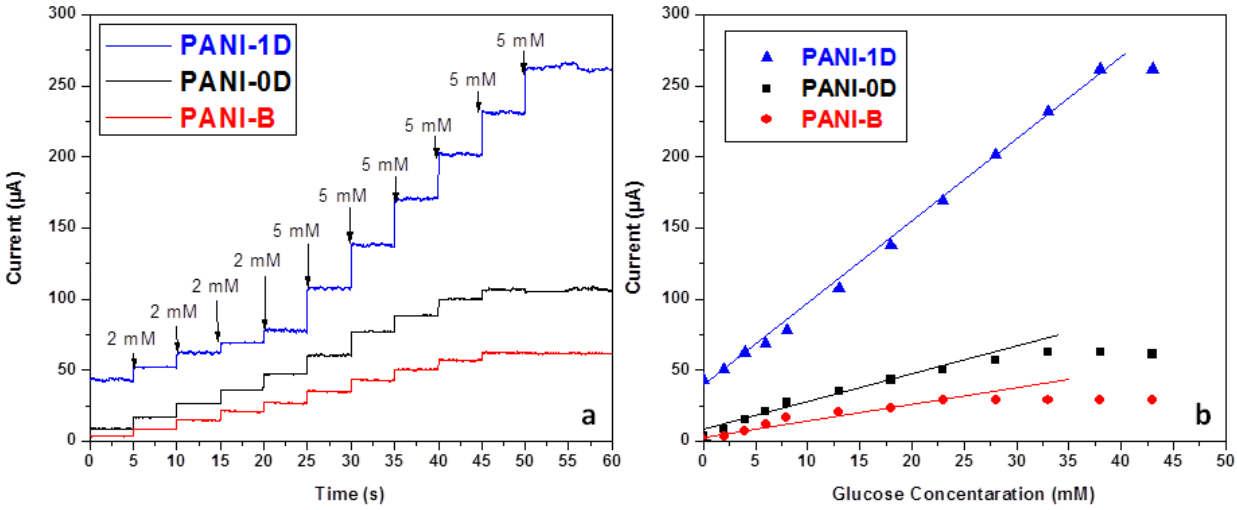

Figure 3. (a) Chronoamperometric response for PANI-1D, PANI-0D nanostructuresand PANI-B with varying concentration of glucose in PBS buffer (pH=7.2). **(b)** Calibration curves corresponding to the chronoamperometric glucose detection.

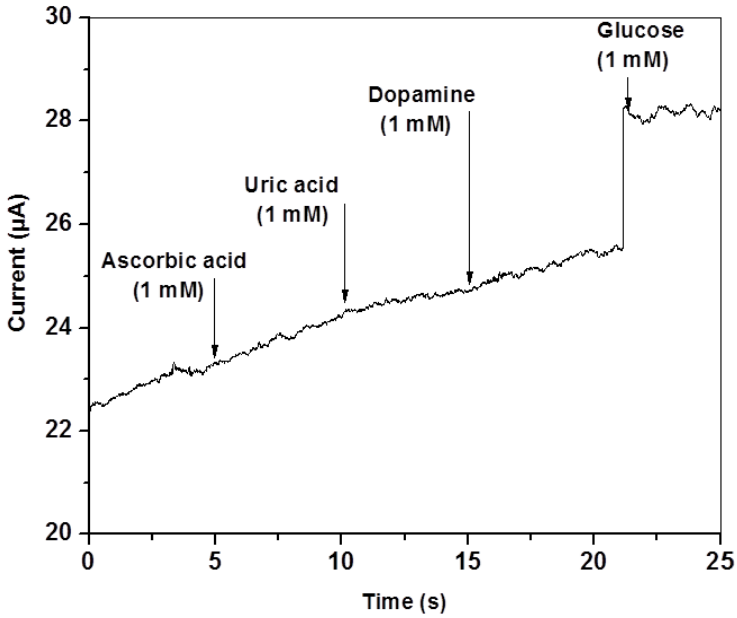

Figure 4. Interference tests of PANI-1D nanostructures with common interfering agents such as ascorbic acid (AA), uric acid (UA), dopamine (DA) and glucose.

4. CONCLUSIONS

ThePANI-NS that were synthesized using 'swollen liquid crystal (SLC)' as soft templates showed high sensitivity, low detection limits and better linear range of detection for theelectrochemical detection of H_2O_2 as well as amperometricbiosensing of glucose. The nanostructured PANI was not only highly sensitive for glucose sensing, but also showed very good selectivity for glucose against common biological interfering agents. Although the concept has been presented within the context of H_2O_2 sensing and glucose sensing, it could be readily extended to other biosensing applications.

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