

Short Communication

Fabrication an Modified Electrode via Ionic-liquid/Bamboo-like Carbon Nanotube/Prussian Blue Nano Particles as a Highly Sensitive Nano-Composite for Detection of H₂O₂

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A nano-composite consisting of bamboo-like multi walled carbon nanotubes and a room temperature ionic liquid (1-butyl-3-methylimidazolium tetrafluoroborate) with prussin blue nanoparticle was prepared and used for modification of glassy carbon electrode. The modified electrode exhibited a pair of well-defined cyclic voltammetric peaks in 0.2 M phosphate buffer solution at pH 7.0. This peak was characteristic of prussian blue nanoparticles (PB-NP) redox couple. The modified electrode showed a very high sensitivity (1.44 $\mu\text{A } \mu\text{M}^{-1}$) toward hydrogen peroxide. Under the optimized experimental conditions, hydrogen peroxide was detected in the concentration range from 1.0×10^{-6} to 3.5×10^{-4} μM with a detection limit of 0.02 μM (S/N=3).

Keywords: Bamboo-Like carbon nanotubes, Ionic liquids, Prussian blue nanoparticles, Modified electrode

1. INTRODUCTION

Application of chemically modified electrodes (CMEs) in the electrochemical determinations has been widely considered as a sensitive and selective analytical method for the detection of trace amounts of biologically important compounds [1-3]. One of the most important properties of CMEs, in comparison to unmodified electrodes, has been their ability to catalyze the electrode process by significant decrease in the needed overpotential [4-6]. With respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion, these electrodes are capable to considerably enhance the selectivity in the electroanalytical methods [7-10].

Carbon nanotube, a new form of elementary carbon, is composed of graphitic sheets rolled into closed concentric cylinders with diameter of nanometers and length of micrometers. Since the discovery of carbon nanotubes in 1991, they have been attracted wide attention in physical, chemical and material science fields because of their unique characteristic involving high electrical conductivity, chemical stability and mechanical strength [11-15]. The subtle electronic properties of carbon nanotubes suggest they have the ability to promote electron transfer reaction when used as the electrode material in electrochemical reaction [16-18]. Meanwhile, it also provides a new way in the electrode surface modification for designing new electrochemical sensors [19-21] and novel electrocatalytic materials. It has been reported that carbon nanotubes modified electrodes were successfully applied to study and determine many biological and organic molecules [22-24].

Prussian blue (PB), as a classical prototype of metal hexacyanoferrates, has been intensively investigated during the past decades. It is well-known for its electrochromic [25-27], electrochemical [28], photophysical [29], magnetic properties [30-31], and potential analytical applications [32-33]. The preparation of PB thin films has attracted much attention of scientists due to their importance in academic research and industrial applications. PB film can be prepared by dip coating [34, 35], electrochemical deposition [36-37], Langmuir–Blodgett (LB) deposition [38], sol–gel technique [39], and so forth. However, among the above-mentioned methods, they generally produced single-component PB films, and the film thickness is also hard to be tuned. The electrostatic layer-by-layer (LBL) self-assembled method, which has been originally introduced by Decher [40], can prepare multi component PB films conveniently because it is based on alternate adsorption of positively and negatively charged ions [41]. To obtain a thin PB film with improved stability and surface uniformity, a number of papers have been contributed to prepare PB multi layers by the alternate deposition of PB and cationic polymers [42-43], inorganic salts [44], enzyme [29] or polyoxometalates [45].

Ionic liquids (ILs) have attracted more considerable attention for their unique chemical and physical properties, such as high thermal stability, high ionic conductivity, negligible vapor pressure, non-flammability, non-volatility and chemical stability [46-49]. Ionic liquids (ILs) have been used widely in catalysis [50-51], extraction and dissolution [52-53], SAMs and nanoparticles [54-55], conductive materials [56], surfactants [57], etc. Furthermore, due to their considerably high ionic conductivity, broad electrochemical window and fast ion mobility [58], ionic liquids have also been utilized as both electrolyte and solvents in the electrochemical preparations of conducting polymers [59-60].

Among multi farious sensors, hydrogen peroxide (H_2O_2) as an important intermediate species or product has been exhibited many biological and environmental processes. The detection of H_2O_2 plays a significant role in many fields including clinic, food, pharmaceutical and environmental analysis [61].

In this paper, a glassy carbon electrode was modified with bamboo like carbon nanotubes-ionic liquids-prussian blue nanoparticles (CNT/IL/PB-MGCE). Then this modified electrode was applied for determination of hydrogen peroxide. Compared with other reported sensors, the (CNT/IL/PB-MGCE) composite film showed much better electrochemical stability, much better sensitivity and larger response current to the reduction of H_2O_2 and better limit of detection. In this sensor we used Bamboo-Like MW-CNT and different multi layer composites that have not reported until now.

2. EXPERIMENTAL

2.1. Reagents

The Bamboo-like Multiwall Carbon Nanotubes (BS-MWCNTs), Potassium Ferricyanide ($K_3Fe(CN)_6$, =99.5%), Hydrogen Peroxide (H_2O_2 ,=30%), Potassium Chloride (KCl, =96.0%), 1-butyl-3-methylimidazolium Tetrafluoroborate, $FeCl_3 \cdot 6H_2O$, HCl (96.0%) and N,N-dimethyl formamide (DMF) were purchased from Sigma-Aldrich Chemicals. All chemicals were of analytical grade and used as received. The buffer solutions were prepared from ortho-phosphoric acid and its salts in the pH range of 2.0–11.0.

2.2. Apparatus

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, The Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System (GPES) software. A conventional three electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the BS-MWCNTs /IL/PB-NP/MGCE were used as the reference, auxiliary and working electrodes, respectively. A Metrohm 691 pH/Ion Meter was used for pH measurements. Also, prepared prussian blue nanoparticle were studied with a particle size analyzer (Zeta- Sizer, Malvern Nano-ZS).

2.3. Synthesis of prussian blue nanoparticle

Prussian blue nanoparticles (PB-Nps) were prepared according to a previously published procedure. Briefly, $K_3[Fe(CN)_6]$ solution in different concentration was slowly added to $FeCl_3 \cdot 6H_2O$ in the presence of H_2O_2 solution under vigorous stirring at room temperature. The resulting dark blue colloidal solution was used as a prussian blue nanoparticles stock solution. The diameter of prussian blue nanoparticles was measured by particle size analyzer [26-27].

2.4. CNT functionalization

BS-MWCNTs were functionalized as follows: 0.5 mg of BS-MWCNTs were dispersed in 25 mL of HNO_3 (35 %) with ultrasonic agitation for 2 hr. The mixture was then diluted with deionized water at 25°C for 0.5 hr and filtered using a 0.45 μm polytetrafluoroethylene filter. The nanotubes were then rinsed with water until a pH above 6 was obtained. The resulting filter cake was dried under IR lamp. Then, 4 mg of the carboxyl functionalized BS-MWCNTs was dispersed in 1 mL DMF with the aid of ultrasonic agitation and used for further experiments [62].

2.5. Fabrication of BS-MWCNTs /IL/PB-Np/MGCE

The preparation of modified GCE was performed by mechanically polishing a glassy carbon electrode with 0.05 μm Al_2O_3 in water slurry then, pouring 2 μL of BS-MWCNTs suspension (0.01 g/mL) onto GCE surface. Then this modified electrode was immersed in a 1:10, 1-butyl-3-methylimidazolium tetrafluoroborate:water for 24 hr. It was washed with water and then immersed in prussian blue nanoparticles to prepare BS-MWCNTs /IL/PB-Np/MGCE.

3. RESULTS AND DISCUSSION

3.1. FTIR characterization of functionalized BS-MWCNTs

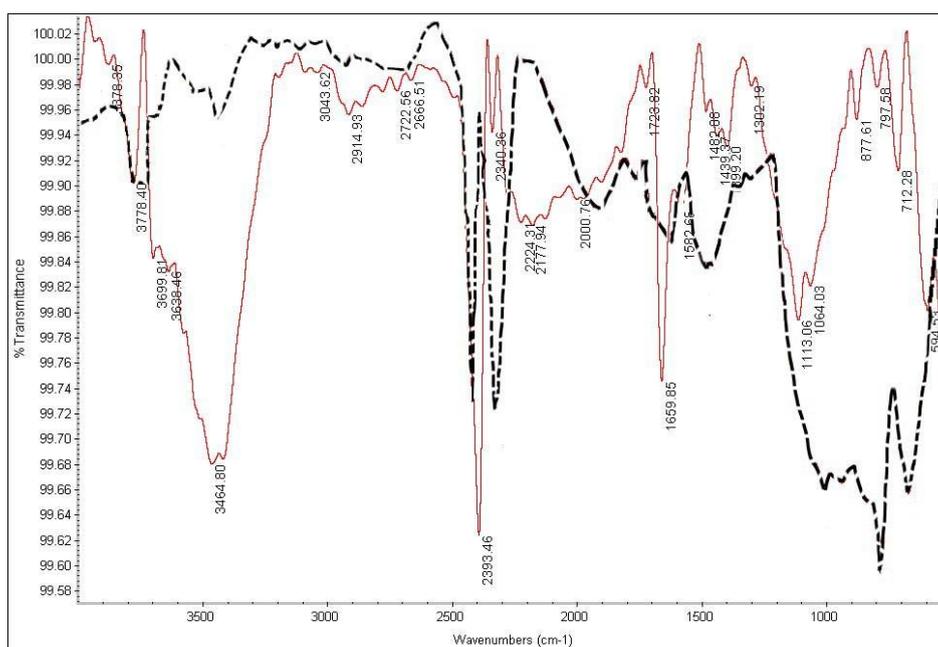


Figure 1. FTIR spectra of acid treated BS-MWCNTs with sonication time of 3 hr (dashed line) and BS-MWCNTs with sonication time of 5 hr (solid line).

FTIR spectroscopy was used to characterize the functional groups on the surface of BS-MWCNTs. Fig.1. shows the FTIR spectrum of acid-treated BS-MWCNTs with sonication time of 3 hr (dashed line) and BS-MWCNTs with sonication time of 5 hr (solid line). In both cases, the peaks at around 1708, 1170 and 3400 cm^{-1} correspond to C=O [63], C–O [64] and O–H stretching vibration [65] of carboxyl group, respectively. This indicates that carboxyl groups were successfully grafted on both types of BS-MWCNTs by acid treatment. Also, three additional peaks at 1640 cm^{-1} , due to C=C stretching vibration [66], 2900 and 3040 cm^{-1} , due to C–H stretching vibration [67], are present in the spectrum of both BS-MWCNTs with different sonication time. However, an increase in the intensity of the carboxyl group corresponding peaks on the surface of BS-MWCNTs with 5 hr of sonication time shows that this BS-MWCNTs was better functionalized.

3.2. Zeta sizer and TEM studies

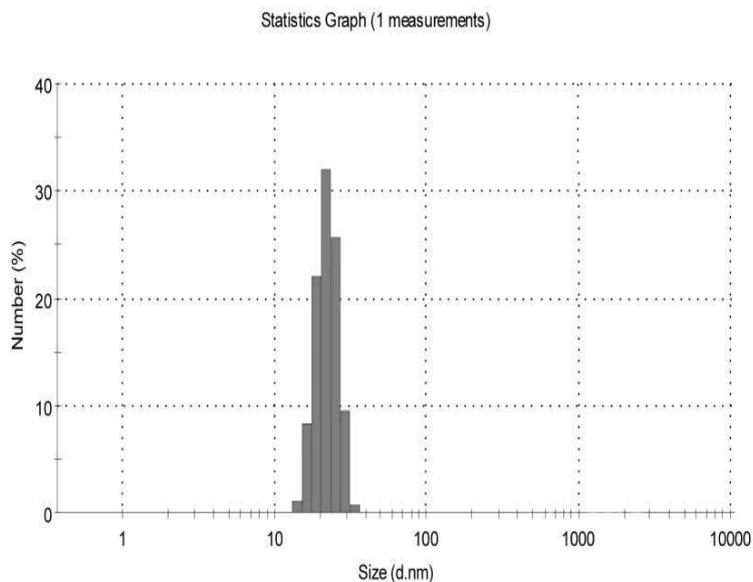


Figure 2. Zeta sizer plot of prussian blue nanoparticles with 4 hr sonication time, 2.5 hr stirring time in 2.0 mg/ml prussian blue solution (pH 5.5.)

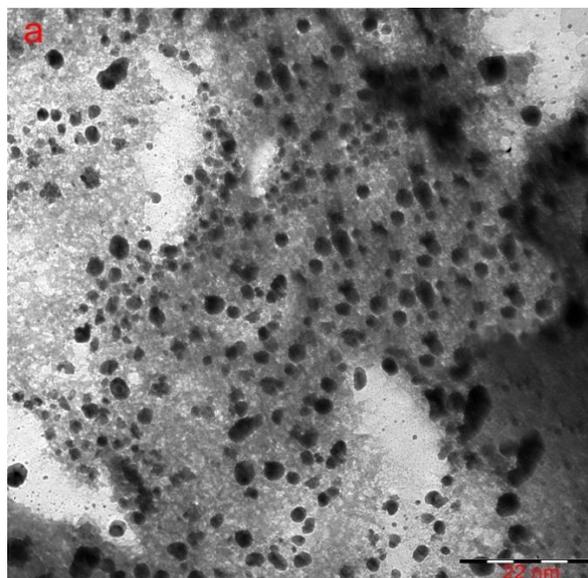


Figure 3. Transmission electron microscope(TEM) image of the structures and size of prussian blue nanoparticles with 4 hr sonication time, 2.5 hr stirring time in 2.0 mg/ml prussian blue solution (pH 5.5.)

The size of Prussian blue nanoparticles were studied by both zeta sizer nanoparticle and TEM image (Fig. 2 and Fig. 3). Zeta sizer nanoparticle showed an approximately 20 nm diameter and TEM image of the resulting PB particles showed spherical nanostructure with an approximately 22 nm

diameters and a relatively narrow size distribution. In this range of size, pb-NP have excellent catalytic activity for direct electron transfer as a mediator [68].

3.3. Electrochemical properties of (BS-MWCNTs /IL/PB-Np/MGCE)

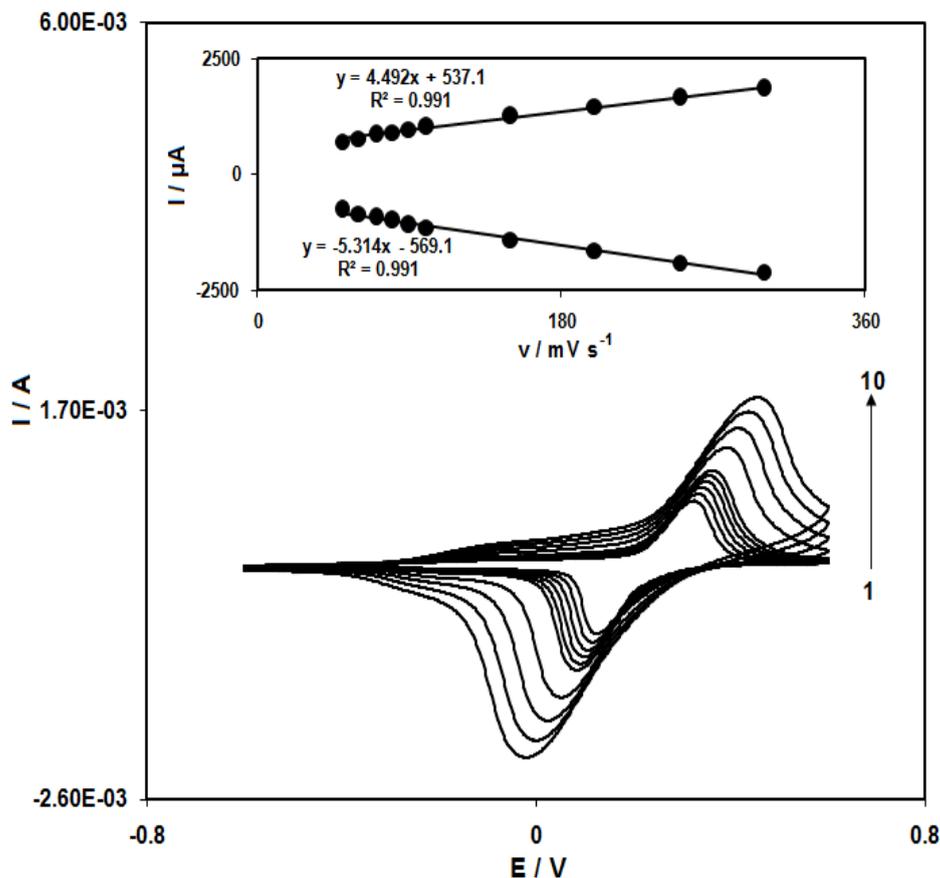


Figure 4. CVs of BS-MWCNTs /IL/PB-Np/MGCE in 0.2 M PBS (pH 7.0), at various scan rates, from inner to outer correspond to 50, 60, 70, 80, 90, 100, 150, 200, 250 and 300 $mV s^{-1}$. Inset: variation of I_p vs. scan rate.

H_2O_2 as an important intermediate species or product has been exhibited in many biological and environmental processes. With respect to the high conductivity of (BS-MWCNTs/IL/Pb-Np/MGCE), it would be interesting to investigate the possibility of the (BS-MWCNTs/IL/PB-Np/MGCE) for constructing a H_2O_2 electrochemical sensor [69].

The (BS-MWCNTs/IL/PB-Np/MGCE) electrode exhibited high electrocatalytic activity toward reduction of H_2O_2 . PB has been found to be a good electrocatalyst for the electroreduction of H_2O_2 , the cathodic current increases remarkably upon the addition of H_2O_2 .

To the best of our knowledge there is no prior report on the electrochemical properties and, in particular, the electrocatalytic activity of (BS-MWCNTs/IL/PB-Np/MGCE) in aqueous media. Therefore, we prepared (BS-MWCNTs/IL/PB-Np/MGCE) and studied its electrochemical properties in a PBS (pH 7.0) using CV (Fig. 4). Experimental results showed reproducible, well-defined, anodic

and cathodic peaks with E_{pa} , E_{pc} and E_0' of 0.32, 0.11 and 0.215 V vs. Ag/AgCl/KCl (3.0 M) respectively. The observed peak of separation potential, $\Delta E_p = (E_{pa} - E_{pc})$ of 210 mV, was greater than the value of $59/n$ mV expected for a reversible system, suggesting that the redox couple of PB in (BS-MWCNTs/IL/PB-Np/MGCE) has a quasi-reversible behavior in aqueous medium. The effect of the potential scan rate on electrochemical properties of the (BS-MWCNTs/IL/PB-Np/MGCE) was also studied by CV. Plots of the both anodic and cathodic peak currents (I_p) were linearly dependent on scan rate in the range of 50–300 mV s^{-1} (Fig. 4 inset), indicating that the redox process of PB at the modified electrode are those anticipated for a surface-confined redox couple [70].

3.4. Cyclic voltammetric behavior of the (BS-MWCNTs/IL/PB-Np/MGCE) electrode

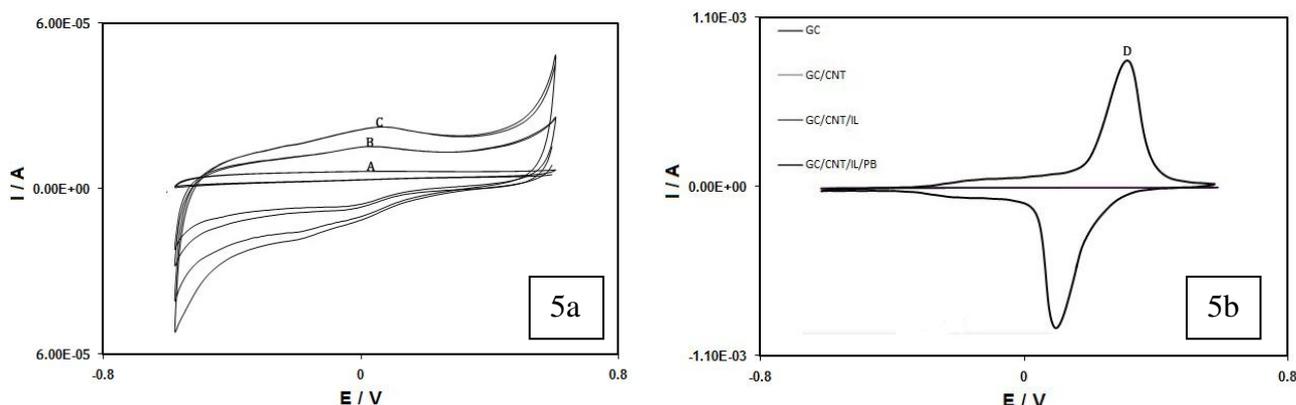


Figure 5a. CVs of different modified electrodes: (A) *MGCE*, (B) *BS-MWCNTs/MGCE*, (C) *BS-MWCNTs/ IL/MGCE*, (b). CVs of *BS-MWCNTs/ IL/ PB-Nps/MGCE* electrode in 0.2 M PBS (pH 7.0).

Cyclic voltammograms of the bare GC, *BS-MWCNTs/MGCE*, *BS-MWCNTs/IL/MGCE* and *BS-MWCNTs/IL/MGCE* electrodes in 0.2 M PBS (pH 7.0) are presented in Fig. 5a. It can be seen that no obvious redox peak can be observed at the bare GC (Fig.5a. curve of A), *BS-MWCNTs/MGCE* (Fig.5a. curve of B) and *BS-MWCNTs/IL/MGCE* (Fig.5a. curve of C) electrodes in the potential range from -0.60 to +0.60 V. The background current at the *BS-MWCNT-MGCE* electrode is larger than that at the bare *MGCE* electrode due to the high surface area of *BS-MWCNTs*. the GC electrode modified with either *BS-MWCNTs* or *IL/MWCNTs* (Fig.5a. curves of B and C, respectively) exhibited no peaks, because they contain no electron transfer. But when PB was immobilized on *BS-MWCNTs/IL/MGCE* modified electrode, a pair of well defined redox peaks was observed (Fig.5b.) [71-75].

3.5. Electrochemical behavior of H_2O_2 at the surface of BS-MWCNTs/IL/PB-Np/MGCE

The utility of the modified electrode for oxidation of H_2O_2 was evaluated by cyclic voltammetry.

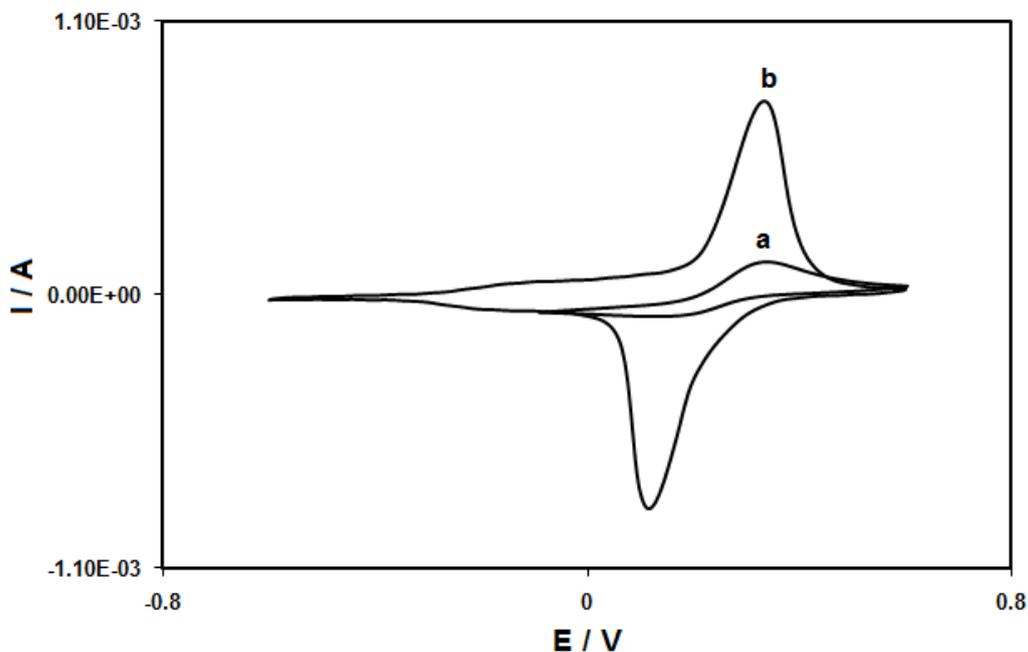


Figure 6. CVs of BS-MWCNTs/IL/PB-Np/MGCE in 0.2 M PBS (pH 7.0) without H_2O_2 (curve a) and with H_2O_2 (curve b).

The cyclic voltammetric responses of a BS-MWCNTs/IL/PB-Np/MGCE in 0.2 M phosphate buffer (pH 7.0), without and with H_2O_2 , are shown in Fig. 6 (curves a and b, respectively). The results show that the sensor produces a large anodic peak current in the presence of H_2O_2 . Such a behavior is indicative of an EC' mechanism [76-77].

3.6. Electrocatalytic determination of H_2O_2

The electrocatalytic peak current of H_2O_2 oxidation at the surface of the modified electrode can be used for the determination of H_2O_2 in solution. Therefore, square wave voltammetry (SWV) experiments were performed using modified electrode in PBS containing various concentrations of H_2O_2 (Fig. 7). The mediated oxidation peak currents of H_2O_2 at the surface of a modified electrode were proportional to the concentration of the H_2O_2 within the ranges $1.0 \times 10^{-6} - 3.5 \times 10^{-4}$ M. The sensors' sensitivities, obtained from the slope of the calibration curve, were $1.44 \mu A \mu M^{-1}$ for BS-MWCNTs/IL/PB-Np/MGCE. The analytical performances of pb for H_2O_2 detection on the BS-MWCNTs/IL/PB-Np/MGCE electrodes are summarized in Table 1.

Table 1. The analytical performances of pb for H₂O₂ detection on the BS-MWCNTs/IL/PB-Np/MGCE electrodes.

Electrode Type	ΔE_p (V)	LOD(μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)	Concentration ranges of H ₂ O ₂	Potential range
BS-MWCNTs/IL/PB-Np/MGCE	210 mV	0.02 μM	1.44	$1.0 \times 10^{-6} - 3.5 \times 10^{-4}$	-0.6 to +0.6

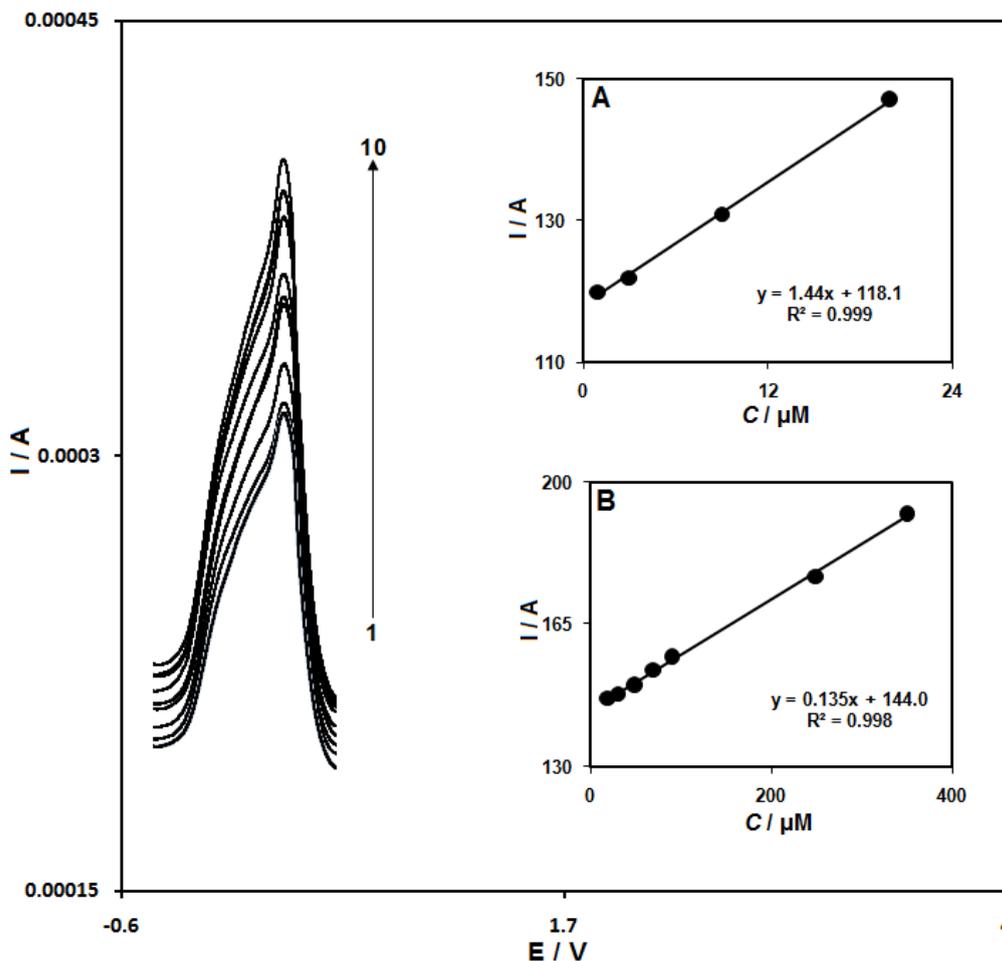


Figure 7. SWVs of BS-MWCNTs/IL/PB-Np/MGCE in 0.2 M PBS (pH 7.0) containing different concentrations of H₂O₂. From inner to outer correspond to 1.0, 3.0, 9.0, 20.0, 30.0, 50.0, 70.0, 90.0, 250.0 and 350.0 μM of H₂O₂. Insets show the plots of the electrocatalytic peak current as a function of H₂O₂ concentration in the ranges of (A) 1.0–20.0 mM, (B) 20.0–350.0 μM .

4. CONCLUSION

Briefly, a new sensor for Hydrogen Peroxide was prepared. Carbon nanotube/ionic liquid electrodes were modified with PB for hydrogen peroxide detection in aqueous buffer solution in concentration range from 1.0×10^{-6} to 3.5×10^{-4} μM with a detection limit of 0.02 μM (S/N=3), successfully. The results showed the natural solubility of PB for modified carbon nanotube ionic liquid

electrode. Excellent sensitivity, low detection limit and two linear ranges toward hydrogen peroxide detection were observed for BS-MWCNTs/IL/PB-Np/MGCE.

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