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A Sensitive Novel Approach towards the Detection of 8-Hydroxyquinoline at Anionic Surfactant Modified Carbon Nanotube Based Biosensor: A Voltammetric Study

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A rapid electrochemical technique was developed to determine 8-Hydroxyquinoline (8HQ). In the current study, the anionic surfactant sodium lauryl sulfate (SLS) was immobilized on the multi-walled carbon nanotube (MWCNT) paste surface to detect 8HQ in phosphate buffer solution (PBS) of pH 7.0. The response of SLS modified carbon nanotube paste electrode (SLSMCNTPE) was inspected *via* cyclic voltammetry (CV), which exhibited a quasi-reversible, diffusion-controlled electrode process for 8HQ. Field emission scanning electron microscopy (FESEM) was adapted to exemplify the electrode surface. The experimental parameters inclusive of variation in pH and scan rate were optimized. This currently prepared sensor displayed excellent stability, reproducibility, repeatability along with elevated sensitivity in CV with the limit of detection (LOD) 1.1×10^{-7} M and limit of quantification (LOQ) 3.9×10^{-7} M. Because of the ease of preparation and regeneration of the developed sensor it extends new prospect for rapid, and sensitive analysis of 8HQ.

Keywords: Carbon Nanotube Paste Electrode, Anionic surfactant, 8-Hydroxyquinoline, Cyclic voltammetry

INTRODUCTION

The heterocyclic aromatic molecule 8HQ is most widely recognized for its antiseptic, preservative, antiperspirant, disinfect, bactericide, deodorant activity, and also it is served as a chelating agent [1,2]. Considering the powerful antimicrobial properties of 8HQ, it is utilized for the production of medicinal, preservative, cosmetic products as well as in the chemical industries. To reduce the harmful effects caused by the drastic usage of cosmetic products containing 8HQ, it should be examined in details [3-4]. Based on the regulations concerned by the European Union Council Directive, the cosmetic products containing 8HQ in their composition should not exceed the maximum allowed concentration of 0.03% (w/w) in non-rinse-off hair care products and 0.3% (w/w) in rinse-off hair care products [5]. Hence, it is essential to detect and determine the 8HQ concentration in commercial products. Some different techniques were reported for the analysis of 8HQ including thin layer chromatography [6], spectrophotometry [7], polarography [8], high-performance liquid chromatography (HPLC) [9-12] and reverse-phase HPLC [13]. The electrochemical technique CV was also used to examine 8HQ with various working electrodes including hanging mercury drop electrode [14], glassy carbon electrode [15], dropping mercury electrode [16,17], carbon paste electrode [18], multi-walled carbon nanotube/Nafion electrode [19]. Compared to the reported works, the present work is carried out with the highly sensitive electrode which is simple, cost-effective and the reagents used to carry out the work will not take to the special treatment. Now, it is of great interest to develop a more sensitive, simple, and cost-effective method to determine 8HQ. The oxidation mechanism of 8HQ is shown in Fig. 1 [15].

Surfactants have been widely used in various electrochemical processes to elevate the electrocatalytic properties of the working electrode. The anionic surfactant SLS is currently magnetizing the researchers for utilizing

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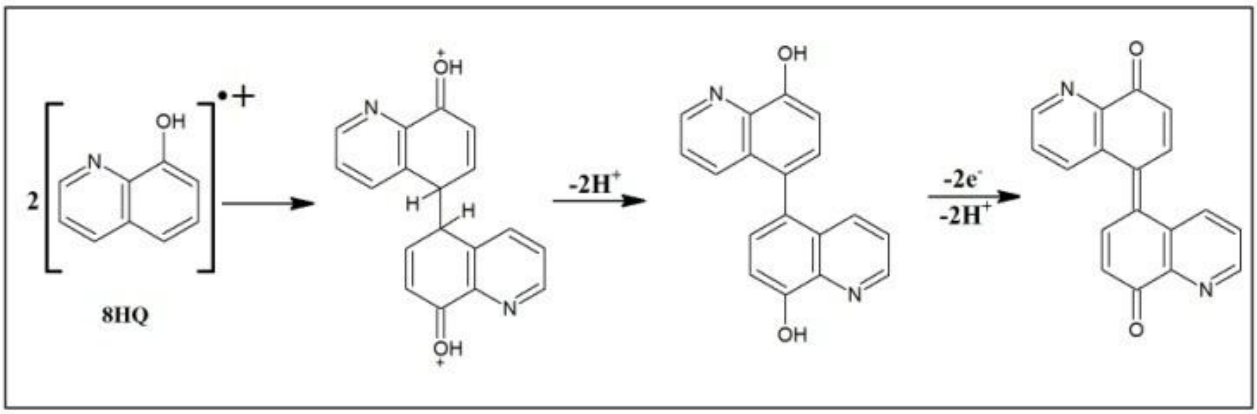

Fig. 1. Oxidation mechanism of 8HQ.

this as a modifier for the construction of bio-sensors. Moreover, it also enhances the accretion of electroactive species at the electrode surface, which increases the rate of transfer of electrons [20-24].

Various kinds of carbon-based materials includes glassy carbon, graphite, carbon nanotubes (CNTs), carbon fibres, and graphenes which are used as a conducting material for the study of electrochemical properties of electroactive moieties [25,26]. Among them, one kind of CNTs, that is, multi-walled carbon nanotubes (MWCNTs), which has gained more advantages over other materials such as broad potential range, electrical conductivity, rich surface chemistry, high catalytic surface, and mechanical strength [27-32]. Hence, this material was chosen for fabrication of the electrode.

The qualities mentioned above for the surfactant and MWCNTs make it a superior combination for the preparation of the sensor. Hence, in the present work, SLSMCNTPE was successfully utilized for the analysis of 8HQ using CV technique. The morphological properties of the modified electrode were compared with the unmodified electrode by studying the FESEM micrographs.

EXPERIMENTAL

Apparatus and Chemicals

The electrochemical characteristics of 8HQ were examined by CV technique *via* computerized electrochemical workstation CHI-6038E (CH Instruments, USA). The entire electrochemical measurements were performed at 25 °C with a three-electrode assembly containing BCNTPE/SLSMCNTPE, a calomel and platinum wire as working, a reference, and a counter electrode, respectively. The surface characteristics of the bare, as well as the modified electrode, was scrutinized using FE-SEM images. The FE-SEM images were collected from DST PURSE Lab, Mangalore University. Silicone oil used as the binder in the preparation of CNT paste was procured from Nice Chemicals, Kerala, India. In the present work, the current values were taken along with the background current.

MWCNTs was purchased from (length 10-30 μm, external diameter 30-50 nm) Sisco Research Laboratory Pvt. Ltd. Maharashtra. All chemicals utilized for this work were of analytical reagent grade. 8HQ was procured from Medilise chemicals, Kerala, and was used as received without further refinement. The stock solution of 8HQ (25×10^{-3}) was prepared using ethanol. The buffer solution of various pHs was prepared by mixing an appropriate volume of 0.2 M sodium dihydrogen phosphate (NaH_2PO_4), and disodium hydrogen phosphate (Na_2HPO_4) (Sigma-Aldrich).

Preparation of Bare and Modified CNTPE

A carbon nanotube paste for the construction of proposed electrode was prepared by carefully mixing 40 wt.% of silicone oil with 60 wt.% of carbon nanotubes through hand-mixing and finely grounded using mortar and

pestle for 20 min until a homogeneous paste was attained. A small portion of the prepared paste was then firmly suffused into the cavity (internal diameter 0.2 mm) of the Teflon tube and rubbed on the tissue paper to acquire the smooth surface. Next, the electrical contact was established by inserting a copper wire through the Teflon tube. Thus, the obtained electrode was applied as BCNTPE. The BCNTPE was modified by immobilizing 10 µl SLS solution onto the electrode surface to obtain the best electrocatalytic response.

RESULTS AND DISCUSSION

Electrocatalytic Performance of the Fabricated Sensor

The CV is an efficient and convenient method to analyze the features of the working electrode surface. For this study, the measurement was carried out for 1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution at a sweep rate of 0.1 V s^{-1}. Figure 2 depicts the CV curve obtained at BCNTPE and SLSMCNTPE for 1 mM $K_4[Fe(CN)_6]$. It can be observed that an enhanced redox peak was acquired for modified electrode compared to the unmodified electrode, owing to the admirable electrocatalytic property of the modifier and the conductive pathway rendered by carbon nanotubes. The electrode exhibits this property due to the enhancement in the active surface area of the fabricated electrode, and it was achieved to be 0.04 cm^2, whereas, for BCNTPE, it was evaluated to be 0.01 cm^2. These values were evaluated using the Randles-Sevcik expression [33,34],

$$I_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} V^{\frac{1}{2}} C \quad (1)$$

where I_p is the peak current, n is the number of transferred electrons, D is the diffusion coefficient, ν is the sweep rate, and C is the concentration of $K_4[Fe(CN)_6]$.

FESEM Examination of BCNTPE and SLSMCNTPE

The surface morphology of BCNTPE and SLSMCNTPE was examined using FESEM micrographs (Fig. 3). Figure 3A describes the surface characteristics of the BCNTPE which contains irregular thread like arrangement of carbon nanotubes, while in SLSMCNTPE (Fig. 3B) the surfactant molecules were adsorbed on the surface of the electrode which provides larger surface area for the electrochemical reaction to take place. Hence, the modified electrode magnifies the electrocatalytic activity of the electrode.

Electrocatalytic Activity of 8HQ at SLSMCNTPE

Cyclic voltammogram was recorded for 1 mM 8HQ in 0.2 M PBS of pH 7.0 in the potential range from -0.1 to +0.8 V at a sweep rate 0.1 V s^{-1}. Figure 4 portrays a CV contour (curve a) obtained for 1 mM 8HQ at SLSMCNTPE with oxidation peak at 0.489 V (I_{pa} = 119.01 µA) and the reduction peak at 0.107 V (I_{pc} = 102.4 µA). Similarly, cyclic voltammogram was recorded at BCNTPE (curve c) where a weak response was observed.

Furthermore, cyclic voltammogram was also recorded for an electrolyte solution without contain the analyte solution (curve b), which does not show any redox peak. 8HQ displayed excellent current response with ΔE_p, that is the deviation of reduction peak potential (E_{pc}) from oxidation peak potential (E_{pa}) and was attained to be much greater than that the theoretical value 0.59 V expected for the reversible electrode process. This data confirms that the electrochemical process taking place at the surface of the electrode was quasi-reversible. The noticeable catalytic reaction associated by the augmentation in the redox peak current is because of the electrostatic interaction between the analyte molecule and the modifier, from which it leads to increase in the concentration of 8HQ around the surface of the fabricated electrode. It confirms that the SLS modifier is a proficient mediator for the transfer of electrons between 8HQ and the electrode. These results proved that the surfactant layer stimulates the electrode process and accelerate the electron transfer kinetics of 8HQ.

Influence of pH on the Current Response of the Sensor

The influence of pH on the cathodic peak current (I_{pc}), and peak potential was probed in the PBS of pH ranges from 5.5-8.0 at the concentration of 1 mM 8HQ. Since the pH of the solution can stipulate the electrochemical activity of the analyte. Figure 5A delineates the CV response of the analyte solution at various pH values. In this investigation,

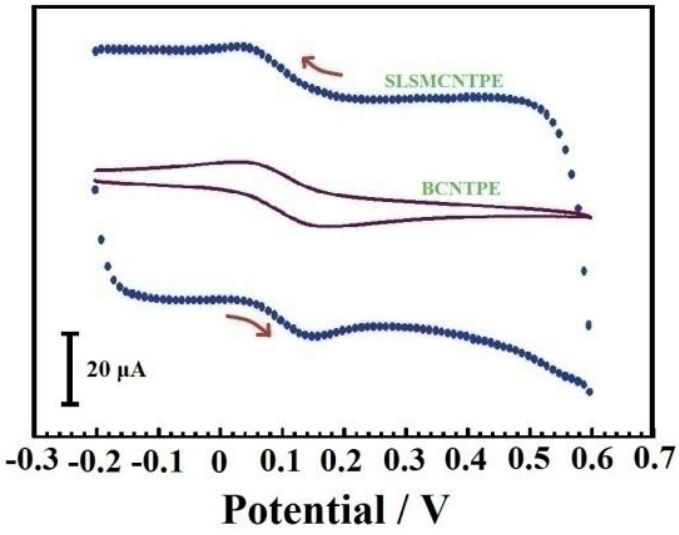

Fig. 2. Cyclic voltammograms of 1mM $K_4[Fe(CN)_6]$ in 0.1 M KCl at BCNTPE and SLSMCNTPE.

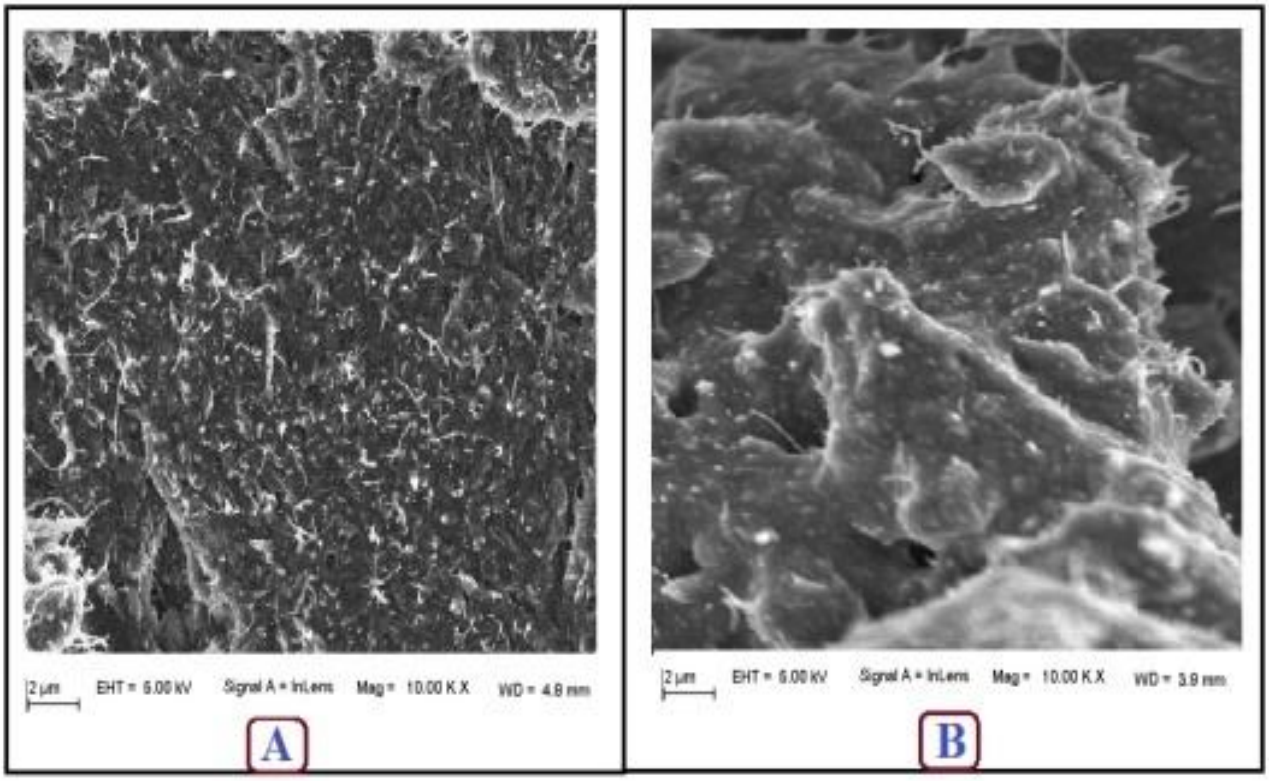

Fig. 3. FESEM micrographs of (A) BCNTPE (B) SLSMCNTPE.

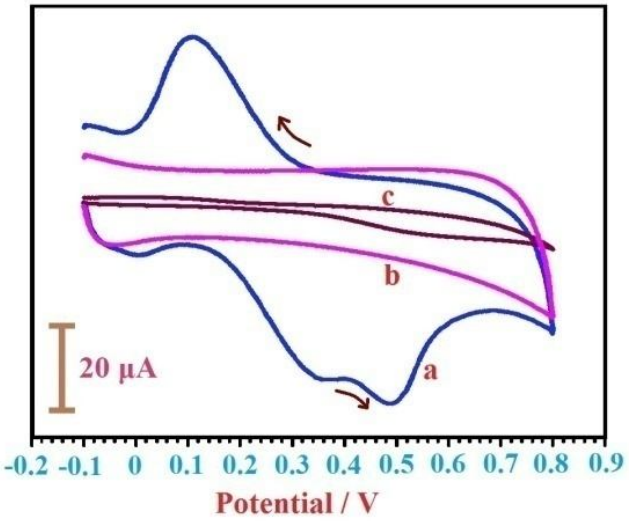

Fig. 4. Cyclic voltammograms of 1 mM 8HQ at BCNTPE (curve a) and SLSMCNTPE (curve b) in 0.2 M PBS (pH 7.0). Cyclic voltammogram of 0.2 M PBS at SLSMCNTPE (curve c).

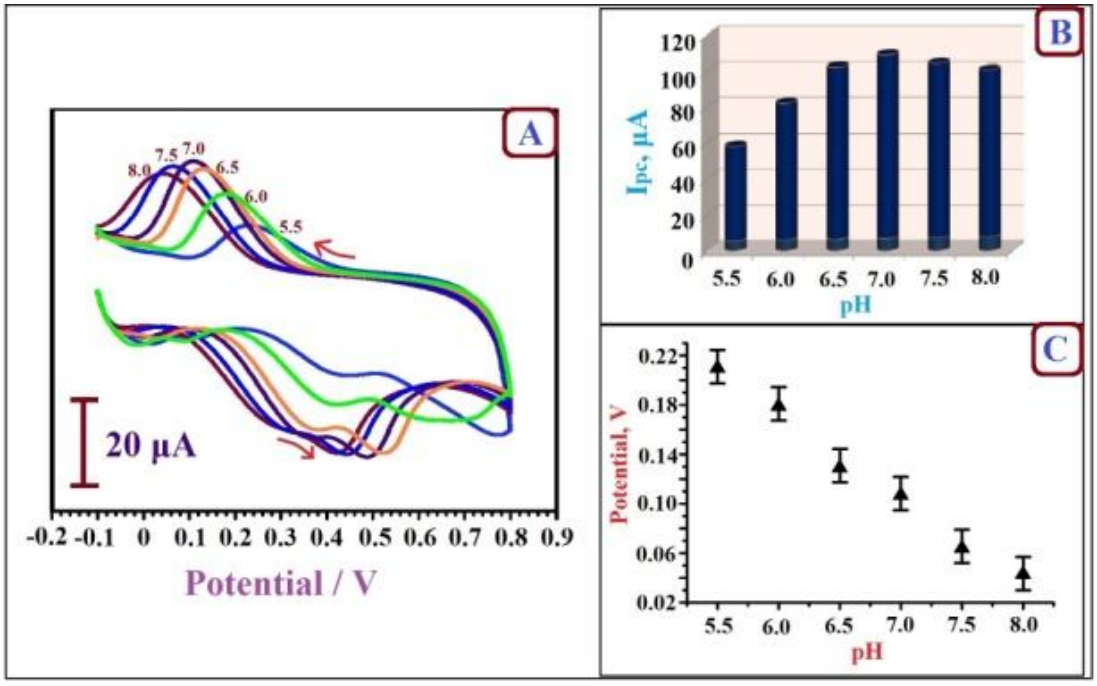

Fig. 5. (a) Cyclic voltammograms of 1 mM 8HQ at SLSMCNTPE in PBS with various pH values (5.5-8.0). (b) Plot of cathodic peak current against different pHs (5.5-8.0). (c) Plot of cathodic peak potential with respect to pH.

the result obtained confirms that in the preferred pH range, the reduction process is pH-dependent. Since the cathodic peak current attains its summit at pH 7.0 (Fig. 5B), it was chosen as the optimal pH for further studies. Besides, the reduction peak potential declined linearly towards negative domain with the increase in the pH of the electrolyte (Fig. 5C). The relationship between the pH of the solution and the cathodic peak potential (E_{pc}) of the concavity can be derived by the equation as E_{pc} = 0.576-0.067 pH (R = 0.990). The slope of this linear segment obtained was 0.067 V/pH, which is in close agreement with the Nernst value 0.059 V/pH. This information suggests the transfer of an equal number of protons and electrons in the electrochemical reaction taking place at the electrode surface [35].

Effect of Sweep Rate on Cathodic Peak Current at SLSMCNTPE

To probe the reaction kinetics, cyclic voltammograms were recorded at SLSMCNTPE with various scan rates from 0.05 V s^{-1} to 0.25 V s^{-1} at PBS of pH 7.0 containing 1mM 8HQ (Fig. 6A). From the CV study, it was observed that there was a progressive augmentation in the redox peak current with a rise in the scan rate along with the considerable movement of oxidation peak potential towards the positive region and the reduction peak potential towards the negative region. In order to explore whether the redox response of 8HQ at SLSMCNTPE is either diffusion or adsorption controlled, CV responses at different scan rates were studied [36]. As delineated in Fig. 6B, the plot of I_{pc} against $\nu^{1/2}$ established excellent linearity with co-relation coefficient R = 0.999 signifying that the reduction process of 8HQ at SLSMCNTPE is controlled by diffusion. This nature was further ratified by plotting the graph of logI_{pc} *vs.* logν (Fig. 6C) based on the equation log I_{pc} = 0.651 logν (V s^{-1}) + 2.690 (R = 0.999). The resultant slope value 0.65, which is almost closer to the speculative value 0.5, confirms the diffusion-controlled nature of the electrode [37].

Repeatability, Reproducibility, and Stability of the Sensor

To examine the reproducibility, the modified electrode was prepared five times in an identical manner, and CV response of 1 mM 8HQ was recorded sequentially. The peak current values were studied. A relative standard deviation (RSD) of 3.40% was attained for this analysis, which signifies an excellent reproducibility of the modified electrode.

The repeatable quality of the prepared electrode was assessed by 1mM 8HQ with the same sensor for 5 consecutive measurements, and the RSD was achieved to be 1.28%, which acknowledges the excellent repeatability of the sensor.

The stability of the sensor was explored by sweeping the electrode for 40 cycles in 1 mM 8HQ solution at a scan rate 0.1 V s^{-1}. Merely a small decrease in the peak current was observed with the signal change of 8.26%, which demonstrate the excellent stability of the modified electrode.

Calibration Plot

The CV technique was applied for the quantitative analysis of 8HQ under optimal circumstances. The cyclic voltammograms were recorded for various concentration profile of the analyte (Fig. 7A). For the study, reduction peak current values were considered. From the obtained data, the calibration graph was plotted by taking the various concentrations of 8HQ in X-axis and peak current values in Y-axis (Fig. 7B). From this plot, we got two linear ranges between 2×10^{-5}-3.5×10^{-4} M and 4×10^{-4}-1×10^{-3} M. The linear regression equation according to the first linear range can be expressed as $I_{pa}(A) = 2.08 \times 10^{-5}$ C + 0.184 (R = 0.990, C in M) and for second linear range $I_{pa}(A) = 6.65 \times 10^{-5}$ C + 0.058 (R = 0.994, C in M). For the evaluation of LOD and LOQ, the first linear range was considered. According to the formula, LOD and LOQ can be written as [38,39],

$$LOD = 3S/B \quad \text{and} \quad LOQ = 10S/B$$

Here, S is defined as the standard deviation of five blank assessments, and B is defined as the sensitivity. By substituting the obtained data in the equation mentioned above, the LOD and LOQ values were achieved to be 1.1×10^{-7} M and 3.9×10^{-7} M, respectively. The sensitivity of the projected electrode is 1.25 A M^{-1} cm^{-2}. These results illustrate that SLSMCNTPE is an apt proposal for the determination of 8HQ.

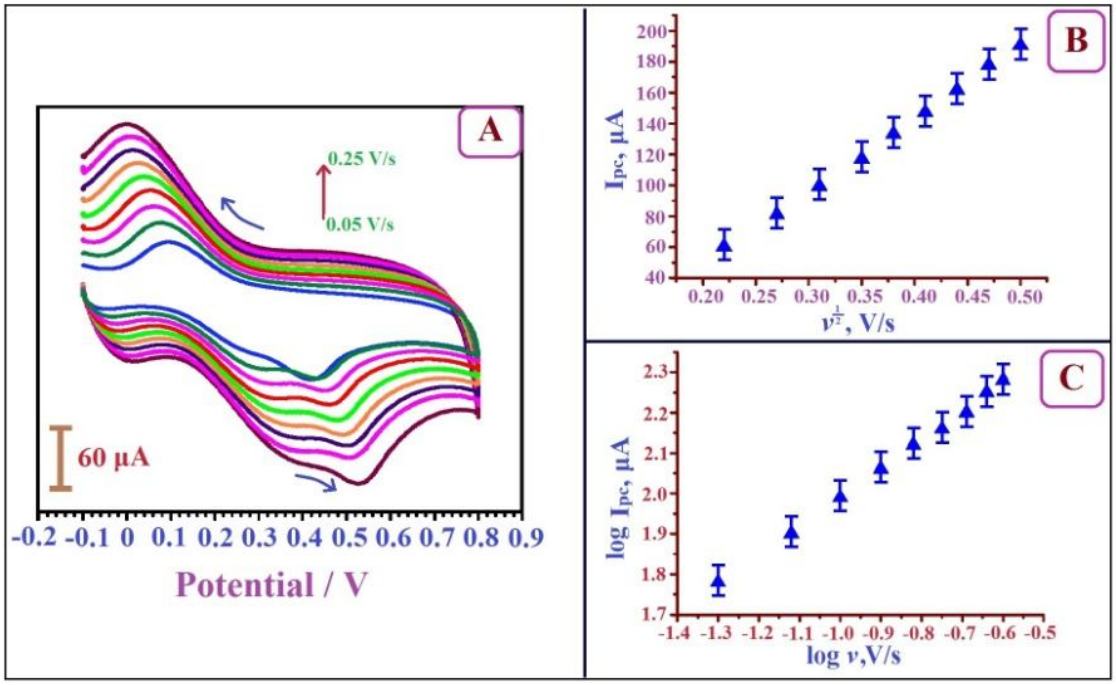

Fig. 6. (A) Cyclic voltammograms of 1 mM 8HQ at SLSMCNTPE in 0.2 M PBS with pH 7.0 at different sweep rates: 0.05 V s^{-1}, 0.075 V s^{-1}, 0.1 V s^{-1}, 0.125 V s^{-1}, 0.15 V s^{-1}, 0.175 V s^{-1}, 0.2 V s^{-1}, 0.225 V s^{-1}, 0.25 V s^{-1}. (B) Plot of cathodic peak current *vs*. square root of sweep rate. (C) Plot of logI_{pc} *vs*. logν.

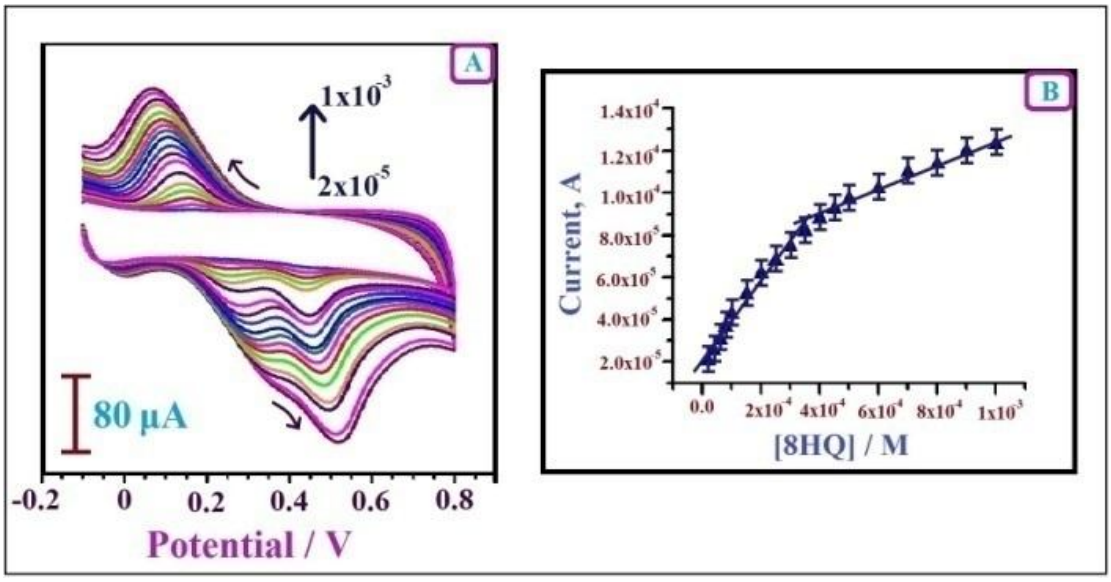

Fig. 7. (A) Cyclic voltammograms of SLSMCNTPE in 0.2 M PBS (pH 7.0) containing various concentrations of 8HQ. (B) Graph of I_{pc} as a function of various concentrations of 8HQ.

CONCLUSIONS

The current endeavour delineates the redox behavior of 8HQ at SLSMCNTPE. This modified electrode manifests excellent catalytic sensing of 8HQ with high sensitivity and low detection limit through the CV technique. The redox reaction taking place at the modified electrode was diffusion controlled and quasi-reversible. It exhibits a peak current which is linear to 8HQ concentration over a specific range in the optimal conditions. The proposed technique offers superiority in simplicity for the preparation of reagents as well as in the handling of apparatus. The significance of the current prepared sensor includes low cost assembly, ease of preparation of the sensor, excellent stability, antifouling properties of the modified electrode, and high sensitivity.

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