Electrochemical determination of capsaicin in pharmaceutical and pepper sauce samples by TiO_2 nanoparticles modified epoxy-graphite electrode

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Introduction

Capsaicin, a lipophilic alkaloid, is responsible for hotness in chili peppers. The presented research focuses on the development of an electrochemical sensor based on epoxy-graphite composite with the modification of Titanium dioxide (TiO_2) nanoparticles for the quantification of capsaicin. The measurements were carried out in glycine buffer at pH 2.5 using the cyclic voltammetry technique. It is observed that carbon based electrodes lead to fouling effect in the cyclic voltammetric measurements of capsaicin. This fouling results in unstable baselines with decreasing net oxidation peak current. In order to overcome this problem, extensive search of electrode modifiers, mainly of nano-technological origin, has been made. From this we observed good behavior in TiO_2 modified electrode. TiO_2 nanoparticles were incorporated into the sensor by adding the nanoparticles into the mixture of epoxy graphite composite during the fabrication of the sensor.

When performing the calibration of the developed sensors, two linear concentration ranges were obtained from 6 to 75 µM (R = 0.99) and 12 to 138 µM; the detection limit was estimated as 5.34 µM and 11.3 µM capsaicin for 1st and 2nd oxidation peak, respectively. The main advantage of the developed sensor is its repeatability with a relative standard deviation (RSD) value of 2.5% after 10 repeated measurements. To the best of our knowledge, our proposed sensor is the first sensor to be developed which does not show fouling effect with capsaicin, this is accomplished through the use of chemical cleaning of the electrode surface which simply involved rinsing the surface in specific media (50% ethanol). This voltammetric sensing platform has successfully been applied to quantify capsaicin in various real samples such as hot pepper sauce and pharmaceuticals.

Construction of Sensors

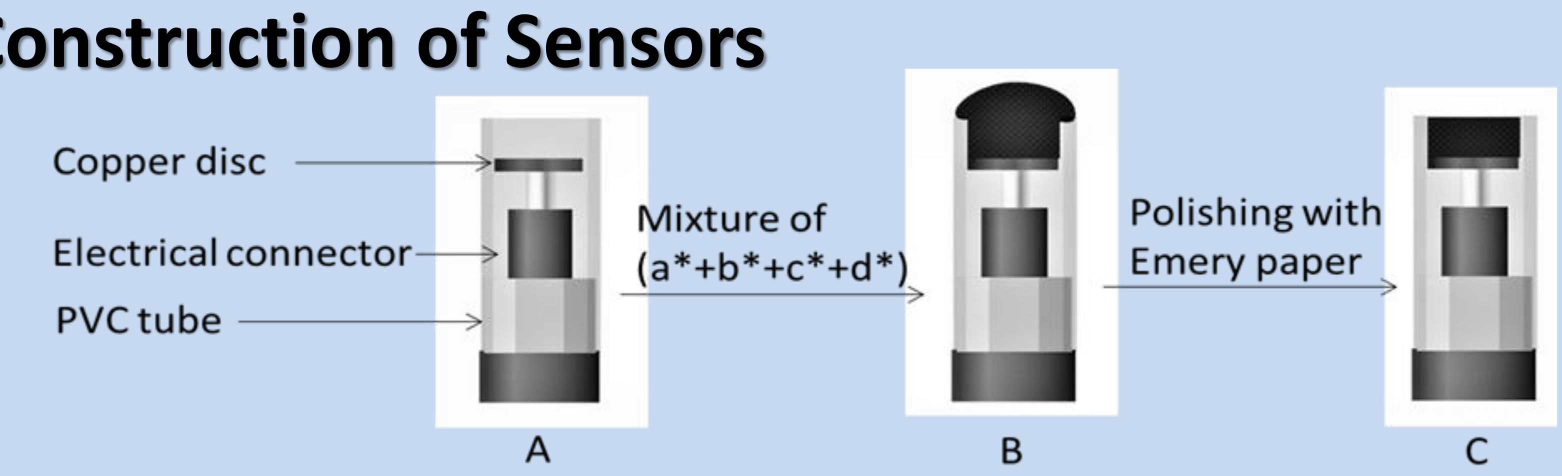
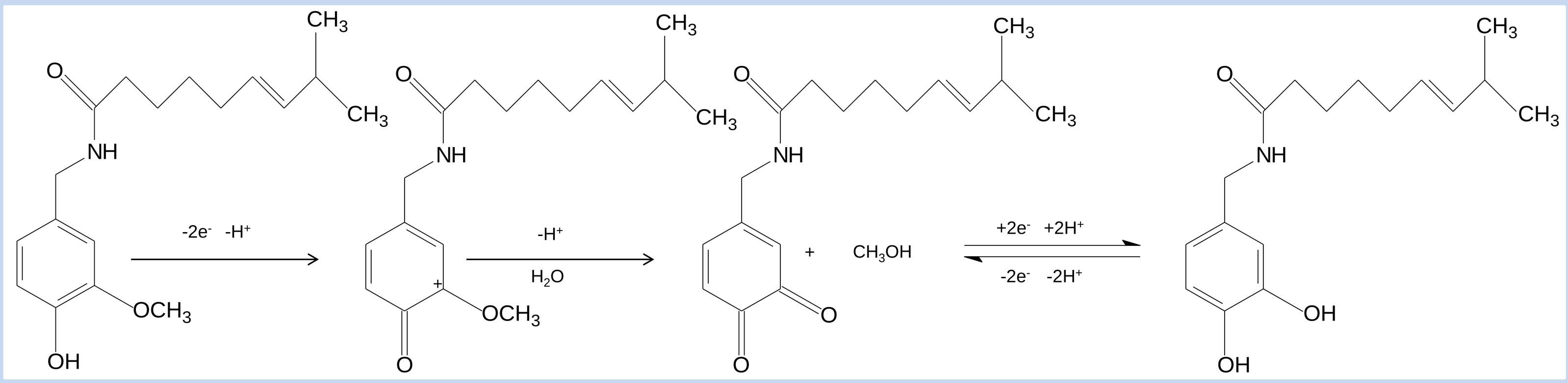


Figure1 : Graphite-epoxy composite electrode construction scheme. a*: graphite powder, b*: Titanium oxide nanopowder, c*: Epoxy resin d*: Hardener.

Reactions involved in the redox process

The redox reactions of capsaicin involves two sets of oxidation reduction reactions as shown in the mechanism which results in two well defined oxidation peak a at potential of 0.70V and 0.48V and corresponding reduction peak at a potential of 0.50 V in the cyclic voltammetric signal.



Scheme1: Mechanism of electrochemical oxidation/reduction of capsaicin.

pH study and selection of Buffer

A pH study was carried out in the pH range of 2 to 6 in the Britton Robinson buffer and a optimum value of pH 2 was found. To avoid extreme acidity on electrode surface a pH of 2.5 and corresponding glycine buffer was selected for the further study.

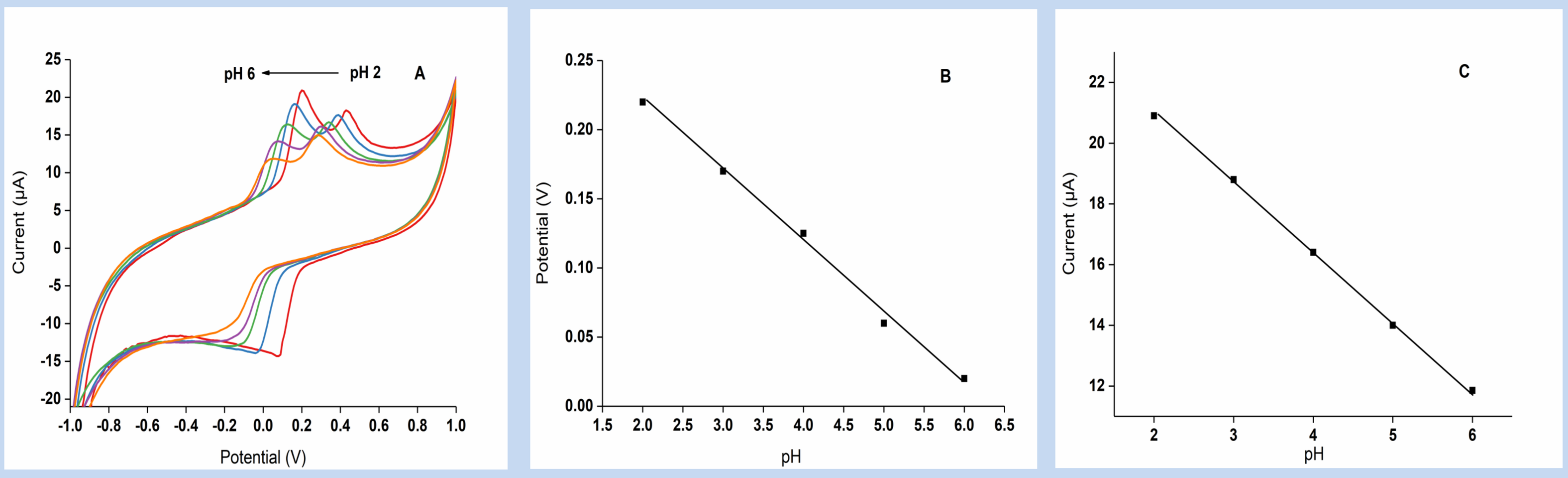


Figure 2: voltammograms for 40 µM capsaicin at different pH (A), Potential of the 1st oxidation peak vs. pH curve (B), Maximum current for the 1st oxidation peak vs. pH curve (C)

Voltammograms : Drawing of calibration curve

Complete voltammograms were recorded for capsaicin by cycling the potential between -.9 V and +1 V vs. Ag/AgCl with a step potential of 0.01 V and a scan rate of 100 mV·s^{-1} as shown in the figure.

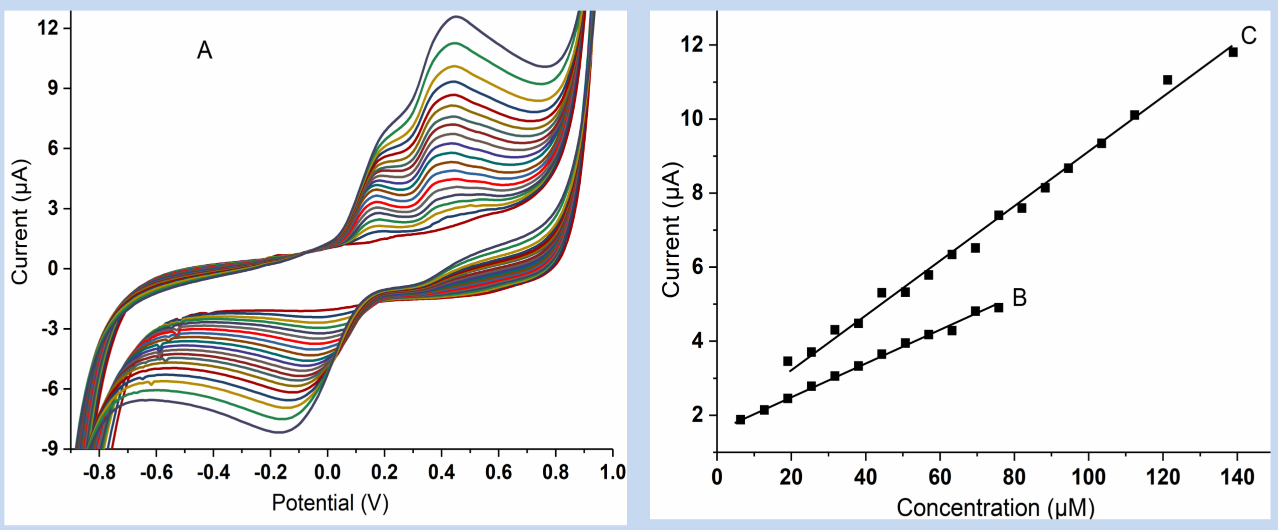


Figure 3: voltammograms in glycine buffer, pH 2.5 at increasing concentration of capsaicin, (6-138 µM) (A); Calibration line for the 1st oxidation peak , (B); for the 2nd oxidation peak (C).

Electrode	Sensitivity, Slope AM^{-1}		linearity R		Limit of detection (µM)		Upper concentration range (µM)	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
TiO_2	0.443	0.077	0.99	0.99	5.34	11.3	75.82	138.93

Table 1: Statistical data of TiO_2 modified electrode from the calibration curve of capsaicin

Stability of the measurements

Stability measurements of capsaicin were carried out by cycling between a standard and a blank and relative standard deviation (RSD) value of around 3.41% was obtained for the sample. The steady value of the blank demonstrate how the fouling is controlled.

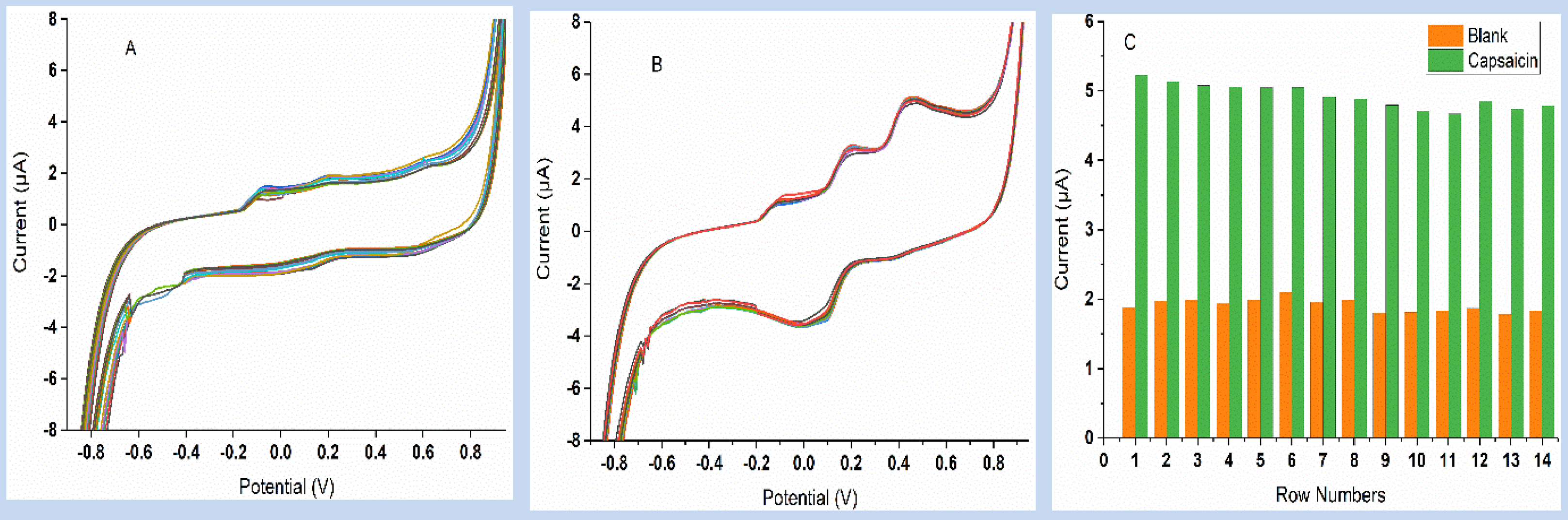


Figure 4: Current Vs. Potential curves for repetitive measurements of blank after each cycle (A), repetitive measurements of 35µM capsaicin in a buffer/capsaicin cycle manner (B), comparisons of blank and capsaicin current measurements at +0.43V (C).

Application to real sample analysis

The developed TiO_2 nanoparticle modified sensor was further implemented to find out capsaicin concentration of a number of sauce and pharmaceutical samples. Capsaicin in the sauce sample was extracted using ethanol solution and this developed sensor could successfully estimate the concentration of capsaicin in the real samples.

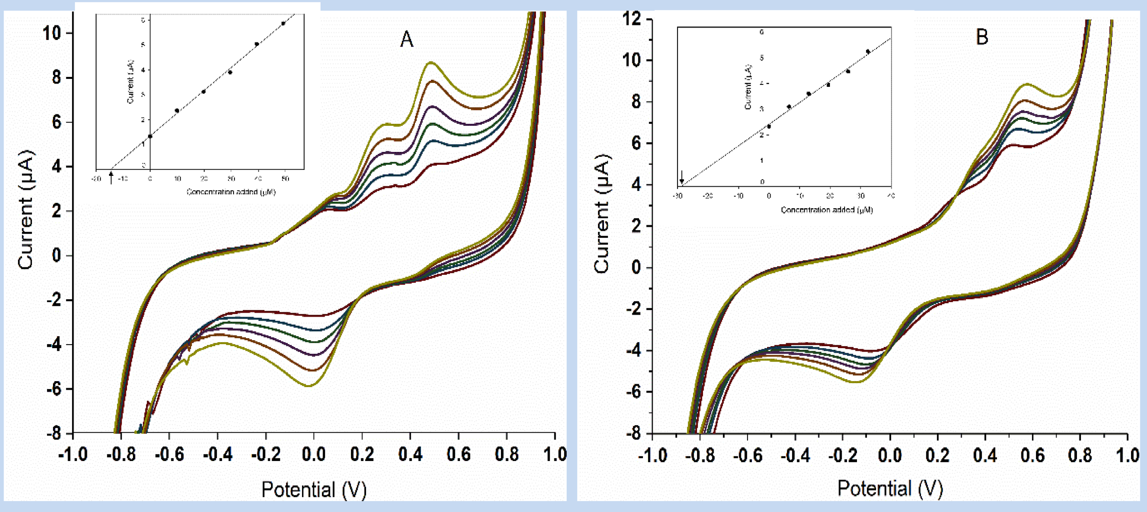


Figure 5: Cyclic voltammetric signals for additions of (A) 10, 20, 30, 40 and 50 µM capsaicin on extracted Delhuerto hot pepper sauce, (B) 6.5, 13, 19.5,26, and 32.5 µM capsaicin on the extracted Alacapsin (pharmaceutical cream).

Pepper samples	Amount of capsaicin determined (µM)	Confidence level (95%)	Actual amount of capsaicin
Delhuerto hot pepper sauce	15.59	±1.49	-
Tabasco habanero pepper sauce	24.68	±2.12	-
Alacapsin (pharmaceutical cream)	29.06	±2.44	30.7

Table 2: Results of calculated concentrations of capsaicin in different real samples

Conclusion

The developed capsaicin electrochemical sensor has shown interesting response features versus capsaicin and can be a good alternative to human-subjective Scoville organoleptic test; it can also be further developed as a portable electrochemical sensor for the estimation of capsaicin content in food and pharmaceutical products.

Acknowledgements

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