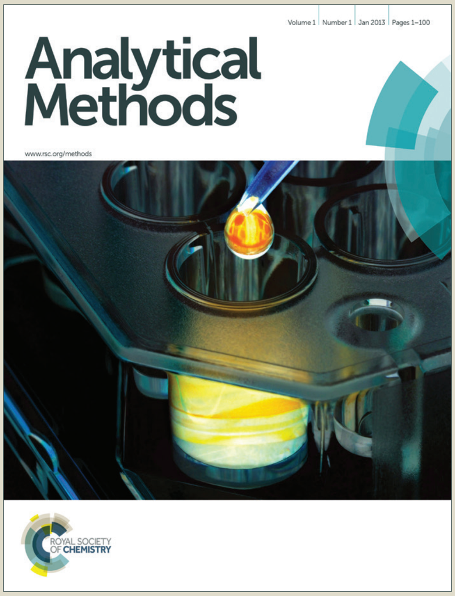
Analytical
Methods

Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Analytical Methods

www.rsc.org/methods

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/methods

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A novel electrochemical sensor for capsaicin based on mesoporous cellular foams

Zhonghua Xue[a], Chenxian Hu[a], Honghong Rao[b], Xuemei Wang[a], Xibin Zhou[a], Xiuhui Liu[a] and Xiaoquan Lu[a*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A novel electrochemical sensor for capsaicin using mesoporous cellular foams (MCFs) as sensitive material is reported. Surface morphology and electrochemical properties of the prepared MCFs modified carbon paste electrode (CPE) were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The proposed modified electrode shows high sensitivity towards the oxidation of capsaicin in 0.1 M perchloric acid solutions (pH 1.0). Under optimized conditions, electrochemical oxidation currents of capsaicin were found to be linearly related to the concentration over the range 0.76 to 11.65 μM with a correlation coefficient of 0.9990, and the detection limit was found to be 0.08 μM at a signal-to-noise ratio of 3. The proposed electrochemical sensor was successfully applied to the determination of capsaicin by using standard adding method with satisfactory results.

Capsaicin (family: Solanaceae), as a major constituent of capsaicinoids, has been widely used in the pharmaceutical industry because of its pharmacological properties.[1-3] We also consume capsaicin daily in our diet and in many foods due to its very pungent flavor. As naturally present component in chilli peppers, capsaicin are more famously known for their sensory attributes of 'hotness' or pungency, aroma and colour, they are lesser known for their health benefits.[4-5] For example, they have high antioxidant activity,[6] anti-tumoral,[7] antibacteria,[8-9] anti-mutagenic,[10] and anticarcinogenic properties.[7,11-12] In recent years, it has attracted great attention of scientists both experimental and theoretical scientists, as it is immensely beneficial for curing biological ailments and improving the overall health of human beings such as protective effects against cholesterol and obesity,[13-14] and analgesics of some diseases.[15] Moreover, the increasing usage of capsaicin in food additives and pharmaceuticals, which make it one of the most interesting issue for the increasing demand in medicine, pharmacy, food science, and human health.

Therefore a simple, sensitive and accurate analytical method for the determination of capsaicin would be useful for the food additives investigations as well as for the increasing usage of capsaicin in pharmaceuticals. In past years, several analytical techniques developed based on spectroscopy,[16-18] chromatography,[19-24] and electrochemical analysis [25-26] have been used for determining capsaicin. Compared to earlier analytical method of Scoville Organoleptic Test,[27-29] chromatography and electrochemical analysis is now widely and routinely used for the determination of capsaicin. However, chromatographic analysis is generally performed using expensive instruments. It also requires extensive labor and analytical resources, and often results in a lengthy turn-around time.[30] Thus, electrochemical detection has been used widely and many approaches have been developed for the determination of capsaicinoids from peppers and various targets,[25, 26] due to its several advantages over other methods in that the instrument is simple and suitable for constructing inexpensive and portable detectors. Recently, nanometer-scale or porous materials have attracted great attention and been widely used in analytical applications. Mesoporous silica materials as a special class of semiconductor nanomaterials are outstanding in their textural characteristics: with high specific surface area, ordered pore structure and narrow pore-size distribution, porous channels, and controlled particle size.[31] Consequently, they have exhibited interest in analytical purposes and this field is rapidly expanding. Moreover, as the current subject of intense research work, electroanalytical sensors based on mesoporous silica have been widely developed and reported.[32-34]

Recently, Liang et al described a simple, rapid, and highly sensitive quantification method for capsaicin using amino-functionalized mesoporous silica, which showing highly sensitive, fast, experimentally-convenient, and low cost for the analysis of capsaicin and was successfully employed to determine capsaicin in hot pepper samples.[30] In an ongoing effort in seeking and preparing mesoporous silica materials sensitive to various targets, it has been found that conventional mesoporous materials such as Mobil Composite of Matter (MCM),[35-38] Santa Barbara (SBA),[39-40] and Hexagonal Mesoporous Silica (HMS) [41-43] are promising substrates for electroanalytical sensors and electrocatalysis. Compared with conventional mesoporous materials mentioned above, Mesoporous Cellular Foams (MCFs) with aerogel like, three-dimensional, continuous and ultralarge-pore structure through incorporation of swelling agent usually exhibit much higher catalytic activity due to their fast mass transfer kinetics, good accessibility for large molecules (e.g. polymers, enzymes).[44-45] These properties make MCFs as an ideal candidate for adsorption and separation, especially in sample pretreatment.

To the best of our knowledge, there is no report on the application of MCFs as substrates for electroanalytical sensors. Herein, in this study, MCFs were firstly employed as an ideal modifier to prepare mesoporous cellular foams modified carbon paste electrode (MCFs/CPE) for the determination of capsaicin. The performance of the proposed electrode was evaluated and discussed by scanning electron microscopy (SEM), electrochemical methods such as cyclic voltammograms (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), square-wave voltammetric (SWV) and electrochemical impedance spectroscopy (EIS). The results exhibited that the as-prepared electrode revealed excellent sensitivity for the detection of capsaicin with superior stability, wide linear range, good reproducibility and recovery.

Capsaicin, graphite powder and paraffin oil were purchased from Shanghai Chemical Co. Ltd. MCFs was synthesized according to the methods described in our previous report.[44] All chemicals were of analytical grade, and were received without any further purification. Twice distilled water from an all-quartz still was used throughout and all the experiments were performed at room temperature.

Electrochemical measurements were performed on an electrochemical detector (model CHI660, CH Instruments Inc.) equipped with a three-electrode system: including a bare CPE or modified CPE as the working electrode, a Pt wire and an Ag/AgCl (saturated KCl) as the auxiliary and reference electrodes, respectively. EIS measurements were performed on a VMP2 Multi-potentiostat (Princeton Applied Research, USA) using an AC signal of 5 mV amplitude at the formal potential of the redox couple over a wide frequency range. The surface morphology of the prepared electrodes was observed through SEM on a JSM-6701F 30 (Japan Electron Optics Co.). The transmission electron microscopy (TEM) image was obtained with a Tecnai G2 F20 U-TWIN (USA) electron microscope.

After optimization of the ratio of graphite powder to binder, the carbon paste was prepared by thoroughly hand mixing the graphite powder and paraffin in the ratio 4:0.7 (w/w) in an agate mortar using a pestle to obtain a homogeneous paste. The CPE was fabricated by packing the resulting carbon paste into the Teflon tube (i.d.=3.00 mm). Then the electrode surface was mechanically polished with a piece of weighing paper and cleaned by distilled water. To obtain the MCFs/CPE, 50 μg of MCFs were dispersed in 1.0 mL of ethanol under ultrasonication to prepare the suspension of the modifier. Then, 4 μL of the above suspension was dropped onto the surface of a carbon paste electrode and then solvent was evaporated at room temperature, resulting the MCFs/CPE was obtained.

The surface morphology and structure of the modified electrode were examined using SEM in order to compare the bare CPE and MCFs/CPE; the images are shown in Fig. 1(a-c). The SEM image of the CPE is illustrated Fig. 1a, indicating the sample is irregularly shaped with the flakes of graphite, which is consistent with that reported previously.[46-47] However, after modified with MCFs, different morphology with a rod-like at nanosize of MCFs/CPE (Fig. 1b) indicates the presence of the MCFs and its immobilization on the surface of the CPE. It is clear that the situation of the surface underwent great changes after the electrode modified. On an individual MCFs, ordered mesopores can be seen, as showed in the SEM image of Fig. 1c, indicating the sample is composed of possessed rodlike structure. Furtherly, a representative TEM images with honeycomb-like of the MCFs was also provided in Fig. 1d, indicating 3D interconnected uniform mesostructures with obvious ultralarge-pore structure, which is in good agreement with those of the MCFs materials in previous report.[44] All these results indicate that the employed MCFs as a promising material have considerable influence on the accessible active areas and lead to an increase for more analyte adsorption in the sample.

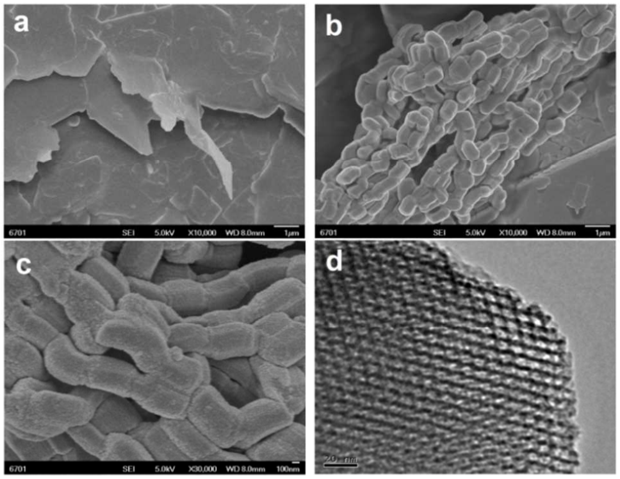


Fig. 1 SEM images of bare CPE (a), MCFs/CPE (b), MCFs (c) and TEM image of MCFs.

CV and DPV experiments were used to characterize the different modified electrodes using 5 mM of $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ (1:1) in 0.1 M KCl as a probe. Fig. 2 shows a typical comparison of the CV and DPV for the bare and modified CPE. For the CV responses (Fig. 2A), the peak-to-peak separations (ΔEp) of probe is 297 mV for the bare CPE (curve a). Compared with bare CPE, the ΔEp decreased to 137 mV for the MCFs/CPE (curve b). In addition, the response currents of the probe also increased than bare CPE. As we expected, the presence of MCFs on the CPE surface could accelerate the electron transfer (ET) between the probe and modified CPE. It also can be seen from Fig. 2B, in which the peak current of the probe on the MCFs/CPE (169.04 μA) is about 3 times of that on the CPE (58.93 μA). It can be attributed to that the MCFs with a rodlike and packed structure enhanced the adsorption properties for the target analyst, resulting exhibited the fastest ET of the probe.

As is well known, EIS is an effective method for studying the interface properties of modified electrodes at very low overpotentials. In this report, EIS was also employed to investigate the charge transfer resistance of the bare and MCFs modified CPE using 5 mM $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ (1:1) in 0.1 M KCl solution, as shown in Fig. 2C. The impendence data were obtained by fitted to the R(Q(RW)) equivalent circuit model (inset of Fig. 2C) using the ZsimpWin program, where *R* is the resistance to charge transfer, *Q* is the constant phase angle element, and *W* is the Warberg-type impedance. The semicircle diameter corresponds to the electron transfer resistance (R_{ct}) which depends on the dielectric and insulating features at the electrode/electrolyte interface. The value of interfacial electron-transfer resistance (R_{ct}) can be estimated to be 2499 Ω and 1039 Ω for bare CPE and MCFs/CPE, respectively, revealing the low ET resistance on the MCFs/CPE. The above results revealed that MCFs/CPE has an obvious improvement effect and a faster charge transfer rate than that of bare CPE. It can be ascribed to the difference of surface area and micro-structures between the two kinds of electrodes.

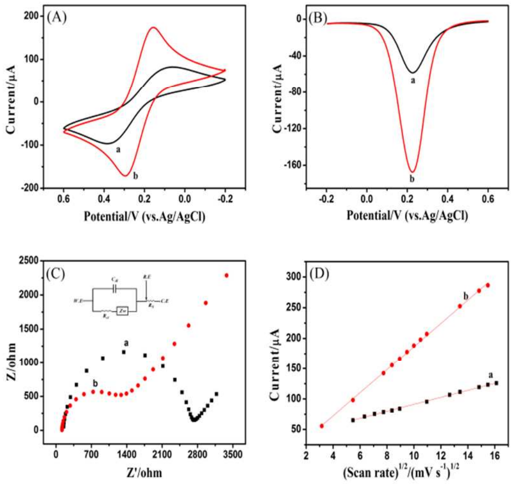


Fig. 2 (A) Cyclic voltammogramms, (B) Different pulse voltammogramms of 5.0 mM $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ containing 0.1 M KCl at bare CPE (a), MCFs/CPE (b). (C) Electrochemical impedance spectroscopy measurements of 5 mM $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ in 0.1 M KCl solution on different CPEs. Inset: equivalent circuit model used to obtain equations for the axis of the abscissas of Nyquist diagrams and axis of ordinates of Nyquist diagrams. WE is the working electrode, RE is the reference electrode, and CE is the counter electrode. (D) The relationship between the square root of scan rates and the reduction peak currents of $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ at bare CPE (a) and MCFs/CPE (b).

To prove this hypothesis and explain the difference obtained above, as a probe $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ was employed to investigate the electroactive area of different electrodes. As shown in Fig. 2D, the reduction peak currents of $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ increased linearly with the square root of scan rates. According to Randles-Sevcik equation: [48]

$$i_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} C_0 v^{1/2}$$

Where *n* is the number of electrons involved (n=1, in the $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ redox system), *A* is the geometric area of the electrode, *D* is the diffusion coefficient of $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ and *C* is the concentration of $K_3[Fe(CN_6)]/K_4[Fe(CN_6)]$ (5.0×10^{-3} mol cm^{-3}), the electroactive area (A) could be determined from the slopes (5.740×10^{-6}, 1.900×10^{-5}) of the two lines at bare and MCFs/CPE, they were 0.1448 and 0.5120 cm^2 for the bare and MCFs/CPE, respectively. Obviously, the MCFs/CPE revealed higher electroactive surface area than the bare CPE. So the enhanced surface contributes to adsorbing more probe molecules and thereby improving its electrochemical response.

To investigate the effect of the MCFs/CPE on the detection of capsaicin, CV and SWV of 50 μg mL^{-1} capsaicin in 0.1 M perchloric acid (pH 1.0) at the bare and MCFs/CPE were measured. As can be seen from Fig. 3A, the CV response of capsaicin at the bare CPE is rather poor and a pair of redox peaks ($E_{Pc1'}$, 0.468 V and $E_{Pa2'}$, 0.525 V) and an anodic peak ($E_{Pa1'}$, 0.696 V) were observed. On the other hand, using MCFs/CPE a well-defined anodic peak (E_{Pa1}, 0.724 V) and a pair of redox peaks (E_{Pc1}, 0.443 V and E_{Pa2}, 0.559 V) with a considerable enhancement in the peak current are obtained. The electrochemical behavior of capsaicin at bare and MCFs/CPE is consistent with the previous report and the related electrochemical reaction mechanism of capsaicin can be elucidated in the Scheme 1.[26,31] In addition, the current of Pa1 (28.35 μA) is significantly larger (about 2.17 times) than that of P_{a1}' (13.07 μA), which can be attributed to the increased active surface area of the modified electrode and accumulation of more amounts of capsaicin on the surface of the modified electrode. The results revealed that the modifier of MCFs possesses remarkable enhancement effects toward the oxidation of capsaicin. Further investigations on the SWV of 50 μg mL^{-1} capsaicin at the bare CPE (curve a) and MCFs/CPE (curve b) were performed and provided in Fig. 3B. It is clear that capsaicin exhibited an obvious anodic peak at 0.448 and 0.498 V at the bare CPE and MCFs/CPE, respectively. Notably, the oxidation current of capsaicin at the MCFs/CPE (57.05 μA) is much higher (about 2.65 times) than the bare CPE (21.49 μA), indicating that MCFs/CPE can promote the electro-oxidation of capsaicin, which possibly attributed to the large surface area and unique geometric structure of MCFs/CPE.

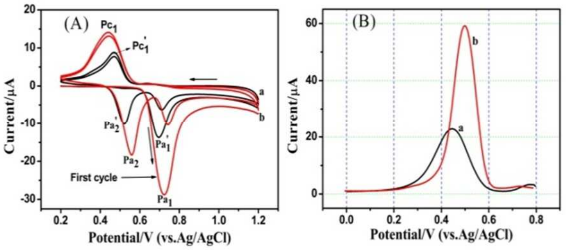


Fig. 3 Cyclic voltammogras and square wave voltammogramms of 50 μg mL^{-1} capsaicin at bare CPE (a), MCFs/CPE (b) containing in 0.1 M perchloric acid, scan rate:100 mV s^{-1}

Electrochemical behavior of capsaicin under different scan rates was further investigated using LSV. Fig. 4 depicts the electrochemical behaviour of 50 μg mL^{-1} capsaicin at the MCFs/CPE in NaAc-HAc (pH 5.8) at different scan rates in the range of 20-200 mV s^{-1}. It is clear that the oxidation currents of capsaicin increase with increasing scan rate. And oxidation peak currents (I_{pa}) have a linear relationship with *v* (r=0.9996, where *v* is the scan rate) (insert A of Fig. 4) with a regression equation as follows, indicating the electrochemical oxidation of capsaicin at the MCFs/CPE was controlled by adsorption.

$$i_{pa} = 0.91764 - 9.99427\nu$$

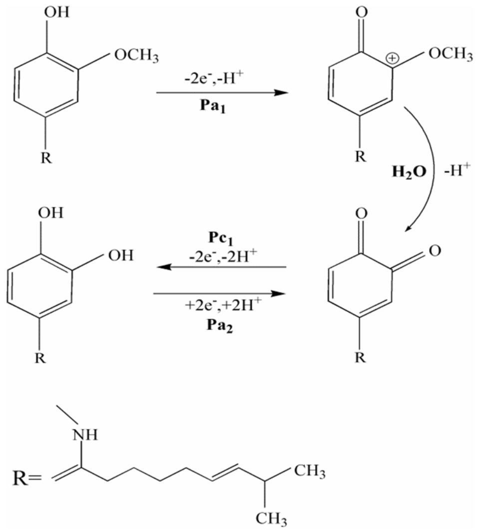
Meanwhile, the effect of scan rate on oxidation peak potential (E_{pa}) of capsaicin was also investigated and provided in insert B of Fig. 4. It also can be seen that the E_{pa} has a linear relationship with lnν (r=0.9917) as showed with a regression equation as follows:

$$E_{pa} = 0.42589 + 0.02631 ln\nu$$

According to Laviron's equation,[49-50] for an adsorption controlled and totally irreversible electrode process, E_{pa} and ν is defined by following equation:

$$E_{pa1} = \mathrm{E}^0 \left(\frac{\mathrm{ET}}{\alpha \mathrm{nF}}\right) \ln \left(\frac{\mathrm{RTk}^0}{\alpha \mathrm{nF}}\right) + \left(\frac{\mathrm{RT}}{\alpha \mathrm{nF}}\right) \ln\nu$$

Where α: the transfer coefficient, k^0: the standard rate constant of the reaction, n: the electron transfer number, v: the scan rate, and E^0: the formal potential. According to the Laviron theory and the equation mentioned above, the value of αn can be easily calculated from the slope of peak potentials versus the logarithm of the scan rate. Here, the slope was about 0.02631, and αn to be 0.86. Generally, α is assumed as 0.5 in the totally irreversible electrode process. Thus, the value obtained for n is 1.72≈2. Hence two electrons are involved in the electrochemical oxidation of capsaicin, which is in good agreement with previous reports.[5, 25, 30]



Scheme 1 Schematic representation of sensing platform for the electrochemical oxdition of capsaicin.

In order to study the effect of pH on the electrochemical properties of MCFs/CPE, the electrochemical process was investigated in 0.1 M perchloric acid solutions of different pH values in the range of 1.0-12.0 with (an increase of 2 pH units) containing 50 μg mL^{-1} capsaicin. Fig. 5A showed the influence of pH on the oxidation of capsaicin at MCFs/CPE. As can be clearly seen, when pH gradually increased from 1.0 to 12, the peak current decreased gradually, and a maximum response is obtained at pH=1.0. For this reason, a pH of 1.0 was chosen for the subsequent experiments. In addition, as two important factors, accumulation time and potential can affect the analytical performance of the MCFs/CPE towards capsaicin. In this work, additional LSV experiments were carried out to investigate the electrochemical response of 50 μg mL^{-1} capsaicin at the MCFs/CPE with different accumulation times and potentials. As can be seen from Fig. 5B, the oxidation peak current of capsaicin increased significantly with the increase of the accumulation time in the range of 20-180 s. The results reveal that long accumulation time can effectively increase the sensitivity of the determination of capsaicin. Whereas further increase of the accumulation time (80-180 s) generates a relatively slow increase of the oxidation peak current, which can be attributed to the saturation of capsaicin at the MCFs/CPE was nearly reached. Furthermore, considering sensitivity and time-saving, 60 s was employed as the appropriate accumulation time for capsaicin detection. The variation of oxidation peak current of target with accumulation potential from -0.2 to 0.3 V is illustrated in Fig. 5C. It is clear that the peak current of capsaicin increased with the increase of accumulation potential value in the range of -0.2 to 0.25 V. However, the peak current of capsaicin decreased gradually as the accumulation potential increased further after 0.25 V, suggesting that a high accumulation potential is helpful for capsaicin detection. Obviously, 0.25 V was chosen as the optimal accumulation potential in the present work.

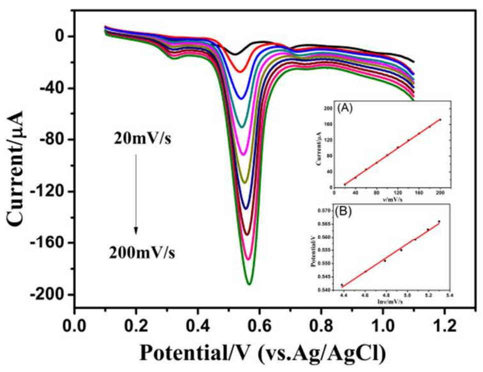


Fig. 4 Linear sweep voltammetry of 50 μg mL^{-1} capsaicin at MCFs/CPE with various scan rates over the range of 20 to 200 mV s^{-1} in NaAc-HAc solution (pH 5.8). Insert (A): plot of peak current versus the natural log of scan rates. Insert (B): plot of peak potential versus the natural log scan rate.

It is well known that the DPV technique exhibits lower background, higher current sensitivity, a lower detection limit and better resolution than CV.[51] Therefore, under the optimized conditions, DPV was used to the determination of capsaicin at the MCFs/CPE.

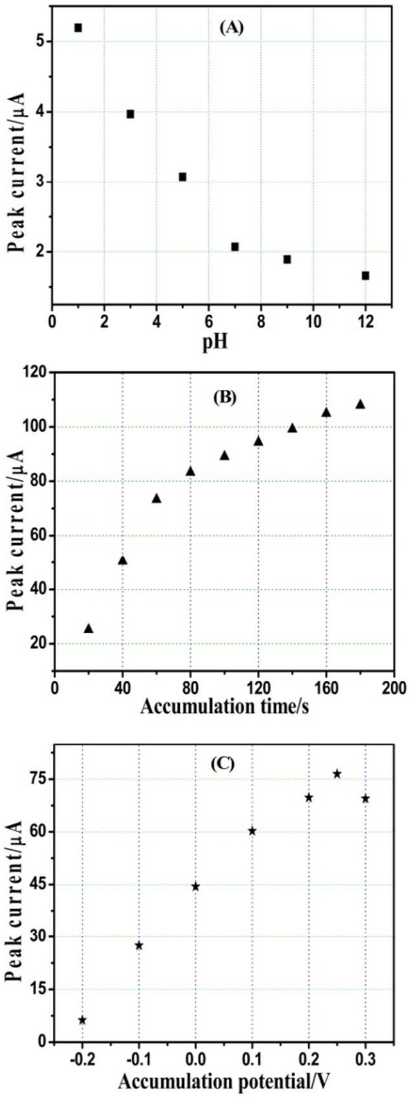


Fig. 5 (A) The effect of pH on the anodic peak current of 50 μg mL^{-1} capsaicin in 0.1 M perchloric acid solutions with different pH values (pH 1.0, 3.0, 5.0, 7.0, 9.0 and 12.0) at MCFs modified CPE with the scan rate of 100 mV s^{-1}. (B) The effect of the accumulation time on the anodic peak currents of 50 μg mL^{-1} at MCFs/CPE with scan rate of 100 mV s^{-1}. (C) The effect of the accumulation potential on the anodic peak currents of 50 μg mL^{-1} at MCFs/CPE with accumulation time of 60 s.

Fig. 6 shows the electrochemical response of MCFs/CPE performed using DPV towards different concentrations of capsaicin in 0.1 M perchloric acid (pH 1.0). As showed in Fig. 6, the oxidation peak current is linearly related to capsaicin concentration, over a range of 0.76 to 11.65 μM L^{-1}, with a correlation coefficient of 0.9990. The detection limit was calculated to be 0.08 μM L^{-1} using the formula $3\sigma/b$, where σ is the standard deviation of the blank (measured 20 times), and *b* is the slope of the calibration curve. The reproducibility of the MCFs/CPE was tested in 0.1 M perchloric acid (pH 1.0) containing 100 μM capsaicin with three times each day for 3 consecutive days. The performance of the as-prepared MCFs/CPE did not change very much. It retained about 96 % of its original sensitivity after 3 days and then decreased slightly to 93 % after 7 days. The results prove that the stability of the sensor is relatively satisfactory. The results of 5 successive measurements for various modified CPE gained by the same method showed a relative standard deviation (RSD) of 3.98 %, indicating that the sensor possesses a remarkable reproducibility.

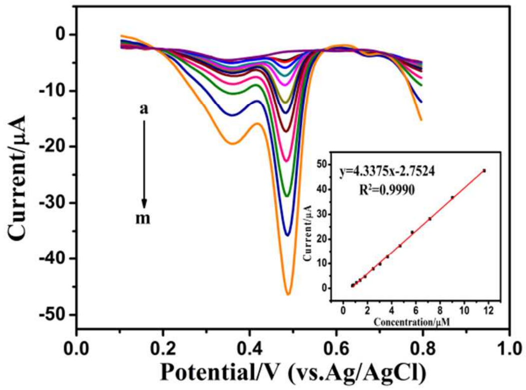


Fig. 6 Differential pulse voltammetry of capsaicin at MCFs/CPE with capsaicin concentrations of (a-m): 0.76, 0.84, 1.09, 1.40, 1.81, 2.48, 3.04, 3.67, 4.70, 5.70, 9.02 and 11.65 μM L^{-1} in 0.1 M perchloric acid solution (pH 1.0). Inset: the plot of the peak current versus concentration of capsaicin.

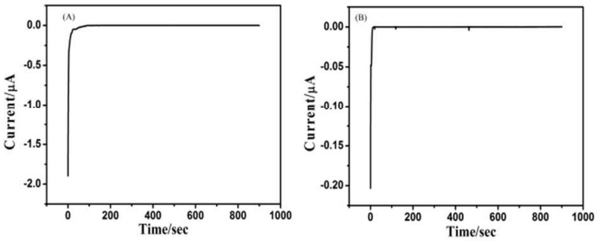


Fig. 7 Amperometric response of 100 μM (A) and 0.1 μM (B) capsaicin at MCFs/CPE for 15 min in 0.1 M perchloric acid of pH 1.0. Applied potential: 0.50 V.

In addition, since the stability of the electrode is an important parameter to decide the fate of a sensor,[47] it was investigated using amperometric technique. To ensure the reliability of the results, the amperometric response of 100 μM and 0.1 μM capsaicin at MCFs/CPE was studied by keeping the oxidation potential a constant at 0.5 V as showed in Fig. 7, respectively. As clearly seen, for either high or low concentration of the sample, both constant amperometric responses were achieved for 15 minutes indicating the antifouling effects and stability of the MCFs/CPE towards capsaicin oxidation.

Furthermore, to confirm the sensitivity and generality of the proposed method, the MCFs/CPE was used for the determination of capsaicin using a standard addition method (n=5). The results are listed in Table 1. As clearly seen, the recovery for the standard addition method was in the range of 96.0-101.1 %, indicating that the MCFs/CPE has good accuracy in analytic application. As well known, one of the most important analytical factors for an amperometric biosensor is the selectivity of the sensor toward the target analyte. Here, the interferences of some common inorganic ions and organic compounds were evaluated. As shown in Fig. 8, there is obvious current response with the addition of 10 mM capsaicin. With the addition of 1.0 M K^+, 1.0 M Mg^{2+}, 1.0 M catechol, and 1.0 M p-chlorophenol, the response current of capsaicin was not obviously decreased. On the contrary, an obvious increased current response was appeared with the addition of 10 mM capsaicin after the interfering species. The result suggests that the influences of these existing species on current responses of capsaicin were negligible and indicates that the proposed method has an excellent anti-interference ability.

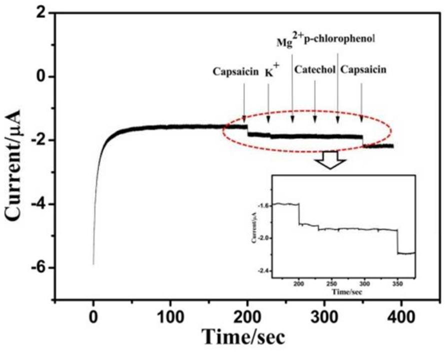


Fig. 8 Amperometric response for successive injection of 10 mM capsaicin and interfering species 1.0 M K^+, 1.0 M Mg^{2+}, 1.0 M catechol, 1.0 M p-chlorophenol in 0.1 M perchloric acid solution (pH 1.0) with stirring, the working potential was 0.50 V. Insert: magnifying figure of amperometric response for the addition of interfering species.

Table 1 Recovery results for capsaicin in standard sample.

Initial capsaicin concentration (μM)	Standard capsaicin Added (μM)	Founded (μM) RSD < 2.8%	Recovery (%)
1.0	0	0.95	96.0
1.0	2.0	2.94	98.0
1.0	4.0	4.88	97.6
4.0	2.0	6.02.	100.3
4.0	4.0	8.09	101.1

The MCFs/CPE was used in several hot pepper power samples to evaluate its practical application. The samples were purchased from local market. 2.5 g of hot pepper power was added to 25.0 mL of methanol and tetrahydrofuran (1:1), and the mixture was sonicated for 1 h. The obtained solution was separated through centrifugation at 5000 rpm for 8 min. The upper-layer solution was collected, and diluted to 50.0 mL with methanol. 50.0 μL of the resulting solution was injected into 10.0 mL of 0.1 M perchloric acid (pH 1.0). The DPV curves were recorded from 0.1 to 1.1 V after 60 s accumulation at 0.25 V. Each sample was determined by three times. The results were listed in Table 2. In order to test the accuracy, the concentration of capsaicine was also detected using HPLC. The results obtained by HPLC and MCFs/CPE were in good agreement, suggesting that this novel method possessed good accuracy and had promising application.

Table 2 Detection of capsaicine in hot pepper samples. Accumulation was at 0.25 V for 60 s.

Samples	By this sensors (μg L^{-1})	By HPLC (μg L^{-1})	Relative error
Die pepper	220	240	8.33%
Cayenne pepper	290	280	-3.57%
Bell pepper	340	360	5.56%

Conclusions

In summary, a novel detecting platform for capsaicin based on a CPE modified with mesoporous cellular foams was firstly explored. The high sensitivity is attributed to the strong adsorption of capsaicin by mesoporous cellular foams and large surface area of the working electrode resulting from MCFs modification. The results show MCFs modified carbon paste electrodes open new opportunities for simple, fast, and sensitive field analysis of capsaicin.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 21265009, 21265018), Program for Chang jiang Scholars and Innovative Research Team, Ministry of Education, China (Grant No. IRT1283), Research Fund for the Doctoral Program of Higher Education of China (20126203120003).

Notes and references

1 M. Hayman, P.C.A. Kam, Capsaicin: A Review of Its Pharmacology and Clinical Applications, Curr Anaesth Crit Care 2008, **19**, 338-343.
2 X.-J. Luo, J. Peng, Y.-J. Li, Recent Advances in the Study on Capsaicinoids and Capsinoids, European Journal of Pharmacology 2011, **650**, 1-7.
3 L. Reyes-Escogido Mde, E.G. Gonzalez-Mondragon, E. Vazquez-Tzompantzi, Chemical and Pharmacological Aspects of Capsaicin, Molecules **2011**, 16 , 1253-1270.

4 R.T. Kachoosangi, G.G. Wildgoose, R.G. Compton, Carbon Nanotube-Based Electrochemical Sensors for Quantifying the 'Heat' of Chilli Peppers: The Adsorptive Stripping Voltammetric Determination of Capsaicin, Analyst 133,**2008**,888-895.

5 E.P. Randviir, J.P. Metters, J. Stainton, C.E. Banks, Electrochemical Impedance Spectroscopy Versus Cyclic Voltammetry for the Electroanalytical Sensing of Capsaicin Utilising Screen Printed Carbon Nanotube Electrodes, Analyst 138,**2013**,2970-2981.

6 D.E. Henderson, A.M. Slickman, S.K. Henderson, Quantitative Hplc Determination of the Antioxidant Activity of Capsaicin on the Formation of Lipid Hydroperoxides of Linoleic Acid: A Comparative Study against Bht and Melatonin, Journal of Agricultural and Food Chemistry 47,**1999**,2563-2570.

7 A.M. Sanchez, M.G. Sanchez, S. Malagarie-Cazenave, N. Olea, I. Diaz-Laviada, Induction of Apoptosis in Prostate Tumor Pc-3 Cells and Inhibition of Xenograft Prostate Tumor Growth by the Vanilloid Capsaicin, Apoptosis 11,**2006**,89-99.

8 M.N. Sathyanarayana, Capsaicin and Gastric Ulcers, Critical Reviews in Food Science and Nutrition 46 ,**2006**,275-328.

9 E.T. Sousa, F. de M. Rodrigues, C.C. Martins, F.S. de Oliveira, P.A. de P. Pereira, J.B. de Andrade, Multivariate Optimization and Hs-Spme/Gc-Ms Analysis of Vocs in Red, Yellow and Purple Varieties of Capsicum Chinense Sp. Peppers, Microchemical Journal 82,**2006**,142-149.

10 Y.-J. Surh, R.C.-J. Lee, K.-K. Park, S.T. Mayne, A. Liem, J.A. Miller, Chemoprotective Effects of Capsaicin and Diallyl Sulfide against Mutagenesis or Tumorigenesis by Vinyl Carbamate and N-Nitrosodiinethylamine, Carcinogenesis 16,**1995**,2467-2471.

11 H.T. Huynh, R.W. Teel, In Vitro Antimutagenicity of Capsaicin toward Heterocyclic Amines in Salmonella Typhimurium Strain Ta98, Anticancer Research 25 ,**2005**,117-120.

12 C. Ganguly, Flavoring Agents Used in Indian Cooking and Their Anticarcinogenic Properties, Asian Pacific Journal of Cancer Prevention 11,**2010**,25-28.

13 M.S. Westerterp-Plantenga, A. Smeets, M.P.G. Lejeune, Sensory and Gastrointestinal Satiety Effects of Capsaicin on Food Intake, International Journal of Obesity 29,**2005**,682-688.

14 R.K. Kempaiah, H. Manjunatha, K. Srinivasan, Protective Effect of Dietary Capsaicin on Induced Oxidation of Low-Density Lipoprotein in Rats, Molecular and Cellular Biochemistry 275,**2005**,7-13.

15 G.C. Morris, S.J. Gibson, R.D. Helme, Capsaicin-Induced Flare and Vasodilatation in Patients with Post-Herpetic Neuralgia, Pain 63,**1995**,93-101.

16 K. Bajaj, G. Kaur, Colorimetric Determination of Capsaicin in Capsicum Fruits with the Folin-Ciocalteu Reagent, Microchimica Acta 71,**1979**,81-86.

17 P.G. Hoffman, M.C. Lego, W.G. Galetto, Separation and Quantitation of Red Pepper Major Heat Principles by Reverse-Phase High-Pressure Liquid Chromatography, Journal of Agricultural and Food Chemistry 31,**1983**,1326-1330.

18 D.S. Pankar, N.G. Magar, New Method for the Determination of Capsaicin by Using Multi-Band Thin-Layer Chromatography, Journal of Chromatography A 144,**1977**,149-152.

19 L. Liu, X. Chen, J. Liu, X. Deng, W. Duan, S. Tan, Determination of Capsaicin and Dihydrocapsaicin in Capsicum Anuum and Related Products by Capillary Electrophoresis with a Mixed Surfactant System, Food Chemistry 119,**2010**,1228-1232.

20 M. Monforte□González, F. Medina□Lara, G. Gutiérrez□Carbajal, F. Vázquez□Flota, Capsaicinoid Quantitation by in Situ Densitometry of Thin Layer Chromatography Plates, Journal of Liquid Chromatography & Related Technologies 30,**2007**,1697-1704

21 Z.A.A. Othman, Y.B.H. Ahmed, M.A. Habila, A.A. Ghafar, Determination of Capsaicin and Dihydrocapsaicin in Capsicum Fruit Samples Using High Performance Liquid Chromatography, Molecules 16,**2011**,8919-8929.

22 Peña-Alvarez, E. Ramírez-Maya, L.Á. Alvarado-Suárez, Analysis of Capsaicin and Dihydrocapsaicin in Peppers and Pepper Sauces by Solid Phase Microextraction–Gas Chromatography-Mass Spectrometry, Journal of Chromatography A 1216 ,**2009**,2843-2847.

23 B.V. Thomas, A.A. Schreiber, C.P. Weisskopf, Simple Method for Quantitation of Capsaicinoids in Peppers Using Capillary Gas Chromatography, ournal of Agricultural and Food Chemistry 46,**1998**,2655-2663.

24 Q.H. Zhang, J.P. Hu, L. Sheng, Y. Li, Simultaneous Quantification of Capsaicin and Dihydrocapsaicin in Rat Plasma Using Hplc Coupled with Tandem Mass Spectrometry, Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences 878,**2010**,2292-2297.

25 R.T. Kachoosangi, G.G.Wildgoose, R.G. Compton, Using Capsaicin Modified Multiwalled Carbon Nanotube Based Electrodes and p-Chloranil Modified Carbon Paste Electrodes for the Determination of Amines: Application to Benzocaine and Lidocaine. Electroanalysis 20(23),**2008**,2495-2500.

26 Y. Yardim, Sensitive Detection of Capsaicin by Adsorptive Stripping Voltammetry at a Boron-Doped Diamond Electrode in the Presence of Sodium Dodecylsulfate, Electroanalsis 23,**2011**,2491-2497.

27 K. De Witte, V. Meynen, M. Mertens, O.I. Lebedev, G. Van Tendeloo, A. Sepúlveda-Escribano, F. Rodríguez-Reinoso, E.F. Vansant, P. Cool, Multi-Step Loading of Titania on Mesoporous Silica: Influence of the Morphology and the Porosity on the Catalytic Degradation of Aqueous Pollutants and Vocs, Applied Catalysis B: Environmental 84,**2008**,125-132.

28 P. Schmidt-Winkel, W.W. Lukens, D. Zhao, P. Yang, B.F. Chmelka, G.D. Stucky, Mesocellular Siliceous Foams with Uniformly Sized Cells and Windows, Journal of the American Chemical Society 121,**1999**,254-255.

29 W.L. Scoville, Note on Capsicums, Journal of the American Pharmacists Association: JAPhA 1,**1912**,453-454.

30 Y. Ya, L. Mo, T. Wang, Y. Fan, J. Liao, Z. Chen, K.S. Manoj, F. Fang, C. Li, J. Liang, Highly Sensitive Determination of Capsaicin Using a Carbon Paste Electrode Modified with Amino-Functionalized Mesoporous Silica, Colloids Surf B Biointerfaces 95 ,**2012**,90-95.

31 H. Rao, X. Wang, X. Du, Z. Xue, Mini Review: Electroanalytical Sensors of Mesoporous Silica Materials, Analytical Letters 46(18),**2013**,2789-2812.

32 M. Hasanzadeh, N. Shadjou, M. Eskandani, M. de la Guardia,

Mesoporous Silica-Based Materials for Use in Electrochemical Enzyme Nanobiosensors, Trac-trends in Analytical Chemistry 40,**2012**,106-118.

33 R.J. Yang, D.Y. Gao, H. Huang, B. Huang, H.Q. Cai, Mesoporous Silicas Prepared by Ammonium Perchlorate Oxidation and Theirs Application in the Selective Adsorption of High Explosives, Microporous and Mesoporous Materials168,**2013**, 46-50.

34 S. Wu, H. Wang, S. Tao, C. Wang, L. Zhang, Z. Liu, C. Meng, Magnetic Loading of Tyrosinase-Fe_3O_4/Mesoporous Silica Core/Shell Microspheres for High Sensitive Electrochemical Biosensing, Analytica Chimica Acta 686,**2011**,81-86.

35 Z.H. Dai, G.F. Lu, J.C. Bao, X.H. Huang, H.X. Ju, Detection of Nadh and Ethanol at Titanium Containing MCM-41 with Low Overpotential, Electroanalsis 19,**2007**,1591-1596.

36 L. Liu, Y. Zhang, L. Zhang, G. Yan, J. Yao, P. Yang, H. Lu, Highly Specific Revelation of Rat Serum Glycopeptidome by Boronic Acid-Functionalized Mesoporous Silica, Analytica Chimica Acta 753 ,**2012**,64-72.

37 W.P. Zhang, C.I. Ratcliffe, I.L. Moudrakovski, C.Y. Mou, J.A. Ripmeester, Distribution of Gallium Nanocrystals in Ga/MCM-41 Mesocomposites by Continuous-Flow Hyperpolarized Xe-129 Nmr Spectroscopy, Analytical Chemistry 77,**2005**,3379-3382.

38 J. Lu, S. Liu, S. Ge, M. Yan, J. Yu, X. Hu, Ultrasensitive Electrochemical Immunosensor Based on Au Nanoparticles Dotted Carbon Nanotube-Graphene Composite and Functionalized Mesoporous Materials, Biosensors & Bioelectronics 33,**2012**,29-35.

39 J. Lin, C. He, S. Zhang, Immunoassay Channels for A-Fetoprotein Based on Encapsulation of Biorecognition Molecules into SBA-15 Mesopores, Analytica Chimica Acta 643 ,**2009**,90-94.

40 El Kadib, P. Hesemann, K. Molvinger, J. Brandner, C. Biolley, P. Gaveau, J.J.E. Moreau, D. Brunel, Hybrid Materials and Periodic Mesoporous Organosilicas Containing Covalently Bonded Organic Anion and Cation Featuring MCM-41 and SBA-15 Structure, Journal of the American Chemical Society 131,**2009**, 2882-2892.

41 S.S. Bhoware, K.R. Kamble, A.P. Singh, Catalytic Activity of Cobalt Containing Mcm-41 and Hms in Liquid Phase Oxidation of Diphenylmethane, Catalysis Letters 133 ,**2009**,106-111.

42 D. Perez-Quintanilla, A. Sanchez, I. del Hierro, M. Fajardo, I. Sierra, Functionalized Hms Mesoporous Silica as Solid Phase Extractant for Pb(Ii) Prior to Its Determination by Flame Atomic Absorption Spectrometry, Journal of Separation Science 30,**2007**, 1556-1567.

43 N. Zhang, G. Li, Z.H. Cheng, X.J. Zuo, Rhodamine B Immobilized on Hollow Au-Hms Material for Naked-Eye Detection of Hg^{2+} in Aqueous Media, Journal of Hazardous Materials 229,**2012**,404-410.

44 X. Wang, J. Liu, A. Liu, Q. Liu, X. Du, G. Jiang, Preparation and Evaluation of Mesoporous Cellular Foams Coating of Solid-Phase Microextraction Fibers by Determination of Tetrabromobisphenol a, Tetrabromobisphenol S and Related Compounds, Analytica Chimica Acta 753,**2012**,1-7.

45 L. Zhang, Q. Zhang, J. Li, Direct Electrochemistry and Electrocatalysis of Myoglobin Covalently Immobilized in Mesopores Cellular Foams, Biosensors & Bioelectronics 26,**2010**,846-849.

46 M.B. Gholivand, L. Mohammadi-Behzad, Fabrication of a Highly Sensitive Sumatriptan Sensor Based on Ultrasonic-Electrodeposition of Pt Nanoparticles on the ZrO_2 Nanoparticles Modified Carbon Paste Electrode, Journal of Electroanalytical Chemistry 712 ,**2014**,33-39.

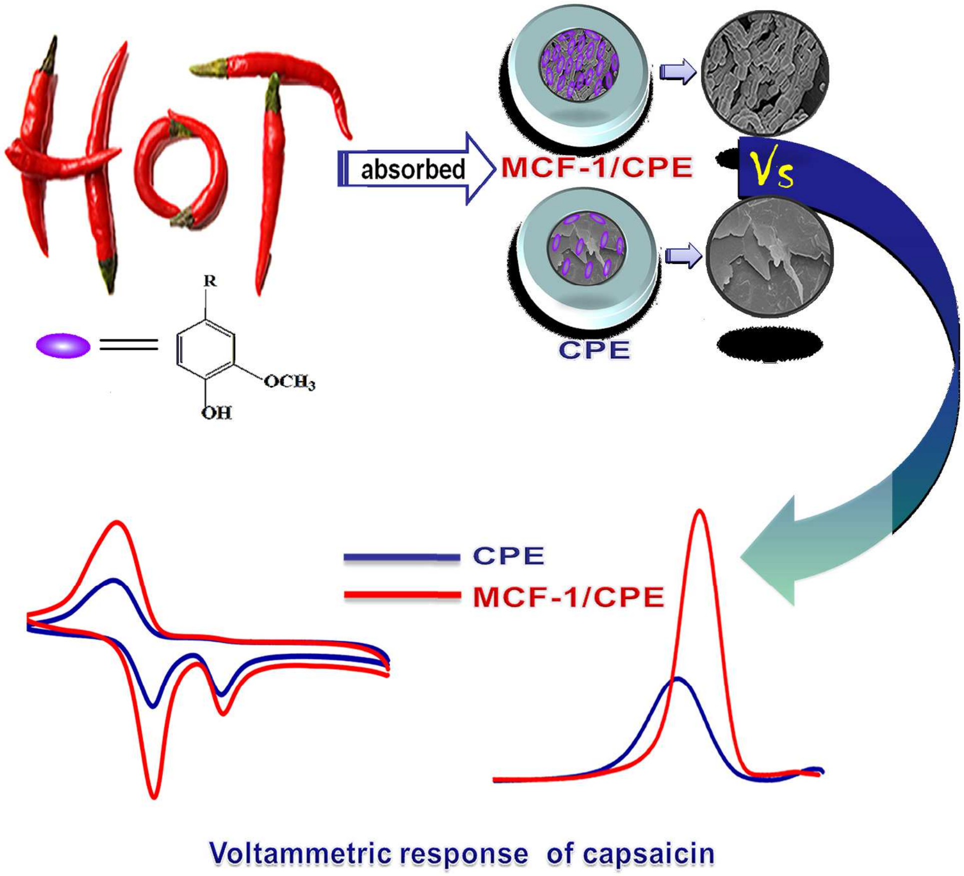
47 T. Thomas, R.J. Mascarenhas, P. Martis, Z. Mekhalif, B.E. Swamy, Multi-Walled Carbon Nanotube Modified Carbon Paste Electrode as an Electrochemical Sensor for the Determination of Epinephrine in the Presence of Ascorbic Acid and Uric Acid, Mater Sci Eng C Mater Biol Appl 33,**2013**,3294-3302.

48 A.J. Bard, L.R. Faulkner, Electrochemical Methodswiley, New York ,**1980**,143.

49 E. Laviron, General Expression of the Linear Potential Sweep Voltammogram in the Case of Diffusionless Electrochemical Systems, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 101,**1979**,19-28.

50 E. Laviron, Adsorption, Autoinhibition and Autocatalysis in Polarography and in Linear Potential Sweep Voltammetry, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 52,**1974**, 355-393.

51 L. Zhang, W.J. Yuan, B.Q. Hou, Nano-Cu/Psa Iii Modified Glassy Carbon Electrode for Simultaneous Determination of Ascorbic Acid, Dopamine and Uric Acid, Journal of Electroanalytical Chemistry 689,**2013**,135-141.



Graphical abstract