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# Highly sensitive electrochemical capsaicin sensor based on graphene-titania-Nafion composite film



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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Capsaicin Graphene Sol-gel titania Modified electrode Voltammetry A highly sensitive electrochemical capsaicin sensor utilizing graphene-doped sol-gel titania-Nafion composite film modified glassy carbon electrode (GCE) is presented. The composite modified GCE is characterized by scanning electron microscopy and its electrochemical properties by electrochemical impedance spectroscopy and cyclic voltammetry. The composite modified GCE facilitates the direct adsorption of capsaicin on the electrode surface via  $\pi$ - $\pi$  interaction between capsaicin and graphene. Furthermore, the present composite modified electrode not only significantly enhances the oxidation peak current, but also decreases its oxidation peak potential, indicating that the graphene in the titania-Nafion composite clearly exhibits good electocatalytic ability to oxidize capsaicin. Under the optimized conditions, the present electrochemical sensor shows a linear response to capsaicin from 0.03 to 10.0  $\mu$ M with a remarkably low detection limit of 8.6 nM (S/N = 3), which is much lower compared to those obtained with previously reported electrochemical sensors. The recovery tests performed for spiked capsaicin in real samples such as Korean hot pepper and red pepper flakes are satisfactory. Thus, the present capsaicin electrochemical sensor could be implemented as a replacement for the human-subjective Scoville organoleptic test, and can also be further developed as a sensitive portable electrochemical sensor for the determination of capsaicin in food and pharmaceuticals.

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#### 1. Introduction

Among a variety of different dishes around the world, hot and spicy foods are gaining popularity in recent years. Capsaicinoids are found in peppers in large amounts, and are known for their pungent taste [1]. The capsaicinoid family consists of 11 components, in which capsaicin (8-methyl-*N*-vanillyl-*trans*-6-nonenamide) is the major component responsible for pungent flavor [2–4]. Not only is capsaicin the main reason for the pungent taste but also it is known for many health benefits. Since capsaicin has high anti-tumoral property [5], anti-oxidation power [6,7], and protective effects against cholesterol [8] and obesity [9], it might be used as the raw material for the new pharmaceuticals. Capsaicin is also be used in self-defensive anti-personnel pepper sprays [10]. Thus, it has become more important to develop a simple and sensitive analytical method for the determination of capsaicin in food and pharmaceuticals.

Up to now, various analytical methods have been developed for the detection of capsaicin. Representatively, the Scoville heat unit, measured through Scoville organoleptic test, has been the typical unit for the level of heat of peppers [11]. In addition to this method, mass spectroscopy [3,12], gas chromatography [13], high-performance liquid chromatography [1,6,14], colorimetry [15,16] and capillary

\* Corresponding author. E-mail address: wylee@yonsei.ac.kr (W.-Y. Lee). electrophoresis [17] have been used for determining capsaicin. However, since the Scoville test is performed by human, it lacks precision and is subjective, due to different sensitivity to the level of pungency for different tasters. Also, other analytical methods have some disadvantages such as expensive instruments, difficult sample preparation, long response time, the need for a skilled operator.

Thus, electrochemical method has attracted much attention out of various detection methods because of quick response time, simplicity, cost-effectiveness, sensitivity and the possibility for on-site field analysis. So many researchers have tried to develop electrochemical methods for the detection of capsaicin based on various electrodes and modified electrodes such as multi-walled carbon nanotube/basal plane pyrolytic graphite electrode and screen-printed electrode [18], boron-doped diamond electrode [19], amino-functionalized mesoporous silica/carbon paste electrode [20], pencil graphite electrode [21], single and multi-walled carbon nanotube/Screen printed electrode [22], gold nanoparticle decorated multi-walled carbon nanotube/GCE [23], and mesoporous cellular foams/carbon paste electrode [24]. Although they demonstrated good sensitivity, stability, wide linear range, and excellent electrochemical performance for determination of capsaicin, there is still needs for the more sensitive analytical methods.

In the present work, GCE modified with graphene-doped sol-gel titania-Nafion composite films has been used for the determination of the capsaicin. To the best of our knowledge, the graphene has not been used for the construction of electrochemical capsaicin sensor. Over the past years, graphene has been widely used in electrochemical sensors and biosensors because it has attractive electrochemical properties such as high electron transfer ability, conductivity, and good electrocatalytic activity, In addition, graphene has a large surface area and excellent adsorptivity since it is consisted of two-dimensional sheet of carbon atoms connected by sp<sup>2</sup> bonds [25,26]. Therefore, graphene can undergo non-covalent interactions with capsaicin molecules, and capsaicin effectively accumulates on the surface of the modified electrode due to  $\pi$ - $\pi$  interaction between the  $\pi$  electrons of aromatic rings in capsaic and the conjugated  $\pi$  electrons of graphene. Meanwhile, Nafion acts as an effective solubilizing agent for graphene and forms a film on the surface of the GCE [27]. Previously, we reported that incorporation of titania-Nafion composite improves the performance of the electrochemical sensors and biosensors because the titania-Nafion composites increases the pore-size (average pore size: 3.14 nm) and improves physical stability compared to pure Nafion film, thereby leading to faster diffusion of analyte into the composite film [28-31]. Therefore, the present graphene-titania-Nafion composite modified GCE can incorporate the advantages of each component, and hence becomes an ideal candidate as a sensitive electrochemical sensing platform for capsaicin. This work demonstrates an excellent analytical performance of the present composite-modified GCE in terms of sensitivity, linear dynamic range, reproducibility and stability, and it can be applied to the determination of capsaicin in real samples.

#### 2. Material and methods

#### 2.1. Reagents

Capsaicin, titanium(IV) isopropoxide (99.999% trace metals basis), Nafion® perfluorinated resin solution (5 wt.% in lower aliphatic alcohol and water, contains 15–20% water), 2-propanol, ethanol, acetic acid, boric acid, phosphoric acid, sodium hydroxide, and hydrochloric acid were purchased from Sigma-Aldrich. Reduced graphene oxide powder was purchased from Graphene-Supermarket (Graphene Laboratories, NY, USA). Water for all solutions was purified using a Milli-Q water purification system (Millipore, Bedford, MA). The stock solution of capsaicin (1.0 mM) was prepared by dissolving in ethanol because capsaicin is not soluble in water. The stock solution was stored in the refrigerator. Working solution was prepared by diluting the stock solution with Britton-Robinson buffer solutions. 0.04 M Britton-Robinson buffer solutions were prepared by mixing solutions of acetic acid, boric acid and phosphoric acid and then adjusting the pH with HCl or NaOH [32,33].

#### 2.2. Instrumentation

Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) experiments were carried out with EG&G 263A potentiostat (Princeton A, NJ, USA) and frequency response detector (Model 1025, Oak Ridge, TN, USA). Electrochemical experiments were performed using a conventional three-electrode system. The working electrode was a bare glassy carbon (GC; diameter, 3 mm) or composite modified GCs, while the counter electrode was a platinum wire, and the reference electrode was an Ag/AgCl (3 M NaCl). Scanning electron microscopy (SEM) images were obtained using field emission SEM (JEOL-6710F, JEOL Ltd. Japan).

#### 2.3. Preparation of the electrochemical sensor

The bare glassy carbon electrode (GCE) was polished with 1.0  $\mu$ m and 0.05  $\mu$ m alumina powder on polishing cloth and then washed with ethanol and deionized-distilled water in an ultrasonic bath for 20 min and dried with air before use. For the preparation of graphene-titania-Nafion modified electrode, titania (TiO<sub>2</sub>) sol was prepared by hydrolysis and condensation by mixing 1 mL of 0.15 M Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>

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dissolved in 2-propanol with 0.1 M HCl and 5 mL of deionized water according to the previous report [28]. The Nafion was diluted with ethanol, and then was mixed with the as-prepared titania sol (1:1, v/v) to prepare the sol-gel titania-Nafion composite solution. A 1.5 mg of graphene was dispersed in 1.0 mL titania-Nafion composite solution. Then, the above mixture was placed into an ultrasonic bath for 60 min. With a micro-injector, 2  $\mu$ L of graphene-titania-Nafion composite solution was hand-cast on the pretreated GCE surface. The modified electrode was dried for 20 min at room temperature and was immersed in buffer solution in order to swell the composite.

#### 2.4. Electrochemical experiments

The composite modified GCE was immersed in the capsaicin solution, and then stirred for 10 min. CV experiments were performed in the potential range of  $0.0 \sim +1.0$  V vs. Ag/AgCl (3 M NaCl). The impedance spectra were carried out in the frequency range of 10 mHz–100 kHz at an applied potential of 0.0 V using an alternating voltage of 5.0 mV in 5.0 mM K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub> (1:1, v/v) solution. ZSimpWin program (Princeton Applied Research, Oak Ridge, TN, USA) has been used to fit the experimental results into equivalent circuit *R*(*QR*)*W* and estimate the diameter of the semicircles.

#### 2.5. Recovery test

Korean hot pepper (Chungyang pepper) and regular red peppers flakes, largely used for flavoring Korean dishes, were chosen for recovery test. The pepper samples were purchased from the local supermarkets. Capsaicin was extracted from the pepper samples prior to the electrochemical analysis similar to the previous report [19]. An aliquot of 1 g of each sample was put into a volumetric flask and dissolved in 20 mL ethanol. The mixture was sonicated for 60 min, then centrifuged at 5000 rpm for 10 min to separate any solids from the mixture. The separated solution was diluted with ethanol (1:1, v/v), then was injected into 0.04 M Britton-Robinson buffer (pH 1.0).

#### 3. Results and discussion

#### 3.1. Characterization of graphene-titania-Nafion composite film

It is found that reduced graphene oxide is easily dispersed in the composite solution composed of sol-gel-derived titania and Nafion (1:1, v/v), which is similar to the case of single- and multi-walled carbon nanotubes in our previous work [30]. The graphene-titania-Nafion composite modified GCE was prepared by simply hand-casting a small aliquot of composite solution onto the surface of a pre-cleaned GCE. Fig. 1 shows the SEM image of the surface of graphene-titania-Nafion composite films. In our previous report [31], it is found that the titania-Nafion composite has three-dimensional micro-pore structure, and thus is highly porous (average pore size: 3.14 nm) as shown in Fig. 1A. When the graphene is further incorporated into the composite, it is obvious that the porous structure is still retained as shown in Fig. 1B. Therefore, the fast diffusion of analyte into and out of the composite film could be possible through the interconnected porous channels in the graphene-titania-Nafion composite films.

#### 3.2. Electrochemical properties of the composite modified GCE

The as-prepared graphene-titania-Nafion composite modified GCE was first examined with EIS and compared to those of a bare GCE and titania-Nafion modified GCE. Fig. 2 depicts the Nyquist plots of EIS obtained at three different electrodes using 5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1, v/v) in 0.05 M phosphate buffer solution (pH 7.0) as a probe. The EIS experimental results were fitted into the R(QR)W equivalent circuit model (inset of Fig. 2) using ZSimpWin program,

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