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Redox behaviour and surface-confinement of electro active species of ginger extract on graphitized mesoporous carbon surface and its copper complex for H_2O_2 sensing

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ABSTRACT

Probing electron transfer behaviour of natural products and trapping of its intermediate species is a challenging research task in the cross-disciplinary area of phytochemistry and electrochemistry. Ginger is a concoction of zingiberene, shogaol and gingerol (responsible for flavour and pungency) which breaks down to zingerone (less pungent) upon drying or cooking. Several reports in the literature deal with the anti-inflammatory and therapeutic uses of ginger, but very scant reports are available on the electrochemical feature of ginger chemicals. Owing to the complex nature, selective recognition of a redox active compound in a phytochemical is a difficult task. Herein, we report an electrochemical study of redox properties of ginger juice on a graphitized mesoporous carbon modified glassy carbon electrode surface by cyclic voltammetry technique (CV) in pH 2 KCl–HCl solution. CV of the modified electrode in presence of dilute ginger solution showed a distinct surface-confined redox peak at $E_{1/2}$, 490 ± 20 mV vs Ag/AgCl with peak-to-peak separation and surface-excess values of 60 ± 2 mV and 20.66×10^{-9} mol cm^{-2} respectively. Physico-chemical characterizations of ginger extract modified electrode by Raman, UV–Vis, FT-IR and TEM reveal electrochemical transformation of 2-methoxyphenol derivatives of ginger compounds such as shogaol and gingerol to respective 1,2-dihydroxy benzene derivatives of gingerol and further anchoring as a surface-confined redox system on the GMC surface via π-π interaction. Ginger based redox system was tuned for complex formation with Cu^{2+} ion and further to sense electro-catalytic activity towards hydrogen peroxide in neutral pH solution.

1. Introduction

Ginger is considered as an excellent therapeutic and culinary natural product. It is widely used as a home remedy to treat various types of diseases and symptoms like stomach problems, nausea, loss of appetite, arthritis, menstrual pain, respiratory tract infections, cough, respiratory, migraine headache, bronchitis, diabetes, burns, pain reliever, insect bites etc [1–5]. Based on the epidemiological investigations, it is well-known in the literature that ingredients of ginger, medicinally important phenolic, can retard the growth of cancerous cell leading to apoptosis of multiple types of cancer including breast, liver, brain, renal and prostate. It is often used as a flavouring agent in foods and beverages, as a fragrance in soaps and cosmetics. It is also highly useful as laxative, anti-gas and antacid [6–8]. The studies show that upon heating, drying or cooking, the pungent components of ginger breaks down to less pungent (sweeter) compound of zingerone as a final compound (Scheme 1) [9–12]. Chemical ingredients present in ginger primarily consist of ortho-methoxyphenolic scaffold which is common among many natural products. Prominent example for this class of compound is curcumin which is the best known medicinally important structure. Indeed, the electrochemical activity of ginger compounds is scantly explored in the literature. In 2016, Chaisiwamongkhol et al. reported electrochemical detection and quantification of gingerol by using adsorptive stripping voltammetry technique with multiwalled carbon nanotube modified electrode (MWCNT) modified electrode [13]. In general, ginger extract is a combination of many reactive species like zingebrene, shogaol and gingerol (Scheme 1). To selectively extract gingerol derivative from the ginger plant, tedious experimental procedure has to be

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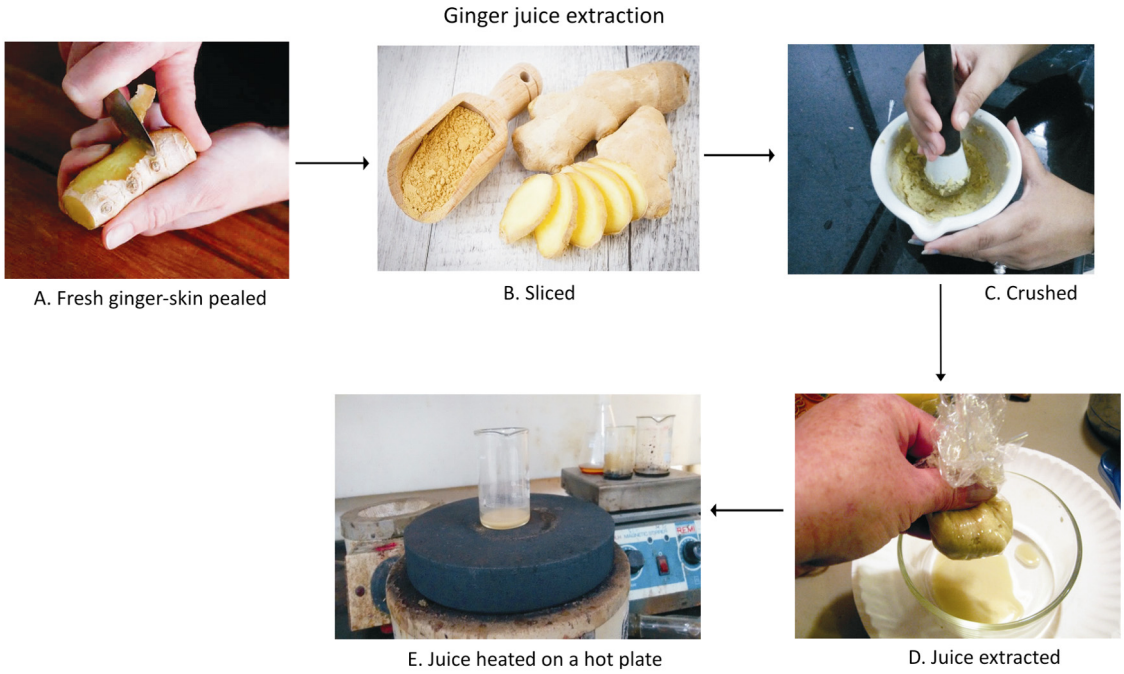

Scheme 1. Typical procedure for the preparation of ginger extract and its heating process.

followed [13]. Herein, we present a simple methodology for selective immobilization of key ginger compounds, zingerone, gingerol, & shogaol as 1,2-dihydroxy benzene derivatives on a graphitized mesoporous carbon (GMC) modified electrode (GCE/GMC@e-ginger, e-ginger = electro-active compounds of ginger) and further to copper complexation studies suitable for the development of hydrogen peroxide sensing in neutral pH.

The ginger compound's redox peak ($E_{1/2} \sim 0.49$ V vs. Ag/AgCl) acquired in this work is found to be highly stable in blank pH 2 HCl–KCl solution. The plausible mechanism for the immobilization of the active compound could be due to the $\pi - \pi$ interaction between graphitic structure-GMC and aromatic ring of the e-ginger derivatives. Various parameters like effect of potential scan rate, underlying carbon and ratio of ginger extract were discreetly studied. Furthermore, the obtained GCE/GMC@e-ginger was subjected to physico-chemical characterizations like Raman spectroscopy, UV–Vis spectroscopy, FT-IR and TEM. In addition, utilizing the selective complexation of copper with 1,2-dihydroxy benzene derivative, a GCE/GMC@e-ginger–Cu^{2+}-Chit complex has been prepared and used as an electrochemical sensor system for the selective detection of hydrogen peroxide in neutral pH. The e-ginger–Cu-complex modified electrode shows a highly selective electro-catalytic reduction signal to H_2O_2 at 0 V vs. Ag/AgCl. Amperometric $i - t$ curve response towards H_2O_2 sensing was also analysed. Effect of interferences with various biochemicals like cysteine (Cys), ascorbic acid (AA), uric acid (UA), nitrite(NO_2^-), glucose (glu) and dopamine (DP) was examined. It is found that the optimized electrode is highly selective towards H_2O_2 sensing and is extendable to real time application.

2. Experimental section

2.1. Chemicals and reagents

Fresh ginger plant was bought from local super market in Vellore. GMC (50 nm size and 99.95% purity), graphite nano powder (400 nm, ~98% purity), carbon mesophorous hydrophilic (99.95%), carbon mesophorous hydrophobic (99.95%), SWCNT (~70% purity on carbon basis, size 0.7–1.1 nm diameter), MWCNT (~90% purity assay; outer diameter size, 10–15 nm; inner diameter size, 2–6 nm; length, 0.1–10 mm),), carbon nano fibre (99.9% purity assay), graphene oxide (98.9%) and $CuSO_4$ were purchased from Sigma Aldrich. Unless otherwise stated a pH 2 HCl–KCl solution was used as a supporting electrolyte throughout the work.

2.2. Apparatus

Cyclic Voltammetry measurements were carried out with a CHI model 660 C electrochemical workstation (USA). The conventional three electrode system consisting of glassy carbon (Tokai, Japan; 3 mm diameter, 0.0707 cm^2 area) in its chemically modified form as a working electrode, Ag/AgCl (in 3 M KCl) as a reference electrode and platinum as a counter electrode with 10 mL working volume was used.

2.3. Procedure

2.3.1. Extraction of ginger juice

First, ginger (weighing 37 ± 0.5 g) was cleaned with double distilled water, peeled and crushed using a motor and pestle (Scheme 2). The obtained paste was filtered with a new sterile muslin cloth and crude juice was collected (15 mL). The juice was heated on a water bath at 50 °C for about 10 min till it is boiled and entire pungency is removed. Both unheated and heated juices were tested in this study. The heat treated ginger extract is used in all the experiments.

2.3.2. Preparation of carbon nano-material modified GCE

GCE was cleaned by using alumina powder followed by electrochemical pre-treatment in pH 7 phosphate buffer solution (PBS) in a potential window of −0.2 to 1 V vs. Ag/AgCl at a scan rate of 50 mV s^{-1} for 10 cycles. 2 mg of carbon nano material (GMC, CNT, Graphene etc.) was taken in 500 μL of ethanol and dispersed in a sonicator for 15 min. 5 μL of the dispersed solution was drop casted on the GCE surface and left for 2 min for air drying. The carbon nanomaterial coated GCE was placed in an electrochemical cell consisting of a mixture of 300 μL of a ginger juice and 9.7 mL of pH 2 HCl–KCl solution as an optimal system along with Ag/AgCl