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Mercapto-ordered carbohydrate-derived porous carbon electrode as a novel electrochemical sensor for simple and sensitive ultra-trace detection of omeprazole in biological samples

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ABSTRACT

We are introducing mercapto-mesoporous carbon modified carbon paste electrode (mercapto-MP-C-CPE) as a new sensor for trace determination of omeprazole (OM) in biological samples. The synthesized modifier was characterized by thermogravimetry analysis (TGA), differential thermal analysis (DTA), transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FT-IR), X-ray diffraction (XRD), elemental analysis (CHN) and N_2 adsorption surface area measurement (BET). The electrochemical response characteristic of the modified-CPE toward OM was investigated by cyclic and differential pulse voltammetry (CV and DPV). The proposed sensor displayed a good electrooxidation response to the OM, its linear range is 0.25 nM to 25 μM with a detection limit of 0.04 nM under the optimized conditions. The prepared modified electrode shows several advantages such as high sensitivity, long-time stability, wide linear range, ease of preparation and regeneration of the electrode surface by simple polishing and excellent reproducibility.

1. Introduction

Omeprazole (5-methoxy-2 [[(4-methoxy-3,5-di-methyl-2-pyridinyl) methyl] sulfinyl]-1H benzimidazole) is a substituted benzimidazole that inhibits gastric acid secretion by covalently binding to the proton pump (H^+/K^+ ATPase) on the surface of gastric parietal cells, and inhibiting the final step in secretion of the hydrogen ions into the gastric lumen [1]. Also, OM is widely used as an antiulcer drug and against other acid-related diseases [2]. This drug is effective in controlling the gastric acidity in Zollinger–Ellison syndrome patients not responding satisfactorily to histamine H_2-receptor antagonist [3]. Formulated as Prilosec© (or Losec©), it is the active component in the world's top-selling pharmaceutical product [4]. Only few methods have been used for determination of OM in pharmaceutical and biological systems, such as high-performance liquid chromatography (HPLC) coupled with UV detector [5–7], spectrophotometric methods [8,9], and capillary electrophoresis [1]. Among the HPLC methods, the HPLC coupled with mass detectors [10–12] have lower detection limits compared to other HPLC methods. Although HPLC has a good sensitivity for determination of OM, the method has many disadvantages such as expensive equipment, time consuming and complex sample preparations. Electrochemical methods have proven to be very sensitive for quantitative determination of organic molecules, including drugs and related molecules in pharmaceutical formulations and biological fluids [13–23]. The electrochemical methods using chemically modified electrodes have been widely used as sensitive and selective analytical methods for the environmental, clinical and bio technical analysis [24,25]. Using of electrochemical sensors and biosensors is increase so much for biological and environmental samples [26–28]. Because they have so many advantages like very low background current (compared to solid graphite or noble metal electrodes), low cost and simple method, large potential window, simple surface renewal process, easiness of miniaturization, good linearity range and good limit of detection [29]. One of the most important properties of CMEs has been their ability to catalyze the electrode process via significant decreasing of over potential respect to unmodified electrode [30]. Recently, the synthesis of bio-compatible materials has attracted scientific attention [31]. One of these materials is carbon derivatives, which has been attracted due to their large specific surface areas, outstanding thermal and chemical stabilities [32]. In particular, nanoporous carbon materials have attracted considerable interest in recent years because these nanoporous materials have numbers of suitable properties, including large surface areas, high adsorption capacities and high thermal and mechanical stabilities. In electrochemistry, the modification of electrode surface is of strong interest in preparing chemically modified electrodes (CMEs) for developing new electrochemical sensors and biosensors with favorable analytical and electrochemical properties [33–35]. Combining the porosity and high surface area of nanoporous carbon open up a range of new applications for these

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materials and could show a new way in the electrode surface modification for designing new electrochemical biosensors.

In this work, for the first time, mesoporous carbon material, which is a biocompatible porous fructose-based material, has been modified with mercapto groups and used as a sensor for electrochemical determination of OM in biological samples. The prepared electrode was successfully applied as a highly sensitive sensor with an acceptable reproducibility and accuracy in the detection of nano-molar amounts of OM in pharmaceutical and biological samples using differential-pulse voltammetry (DPV). The prepared modified electrode showed high reproducibility in both preparation and analytical determination. The introduced sensor compared to previous reports for OM, showed better analytical response characteristics such as detection limit and dynamic linear range.

2. Experimental

2.1. Materials

All reagents including solvents, acids, 3-thiol-propyltriethoxysilane and D-fructose were of analytical grade and purchased from Merck Company (Darmstadt, Germany). Pluronic® F127 triblock (Mw = 12,600, EO106–PO70–EO106) copolymer was purchased from Aldrich Company. Double-distilled water from a Milli-Q purification system (Millipore, Bedford, MA, USA) was used for the preparation of solutions. Plasma and urine samples were obtained from the Clinic of Taleghani Hospital (Tehran, Iran). Stock standard solution of OM (1000 μg mL^{-1}) was prepared in methanol and stored in a refrigerator at 4 °C and brought to ambient temperature just prior to use. The working solutions were prepared daily by diluting the standard solutions prior to use.

2.2. Apparatus

Electrochemical studies were carried out in a glass cell incorporating three electrode configuration containing 25 mL, 0.1 M phosphate buffer solution as running electrolyte, powered by a μ-Autolab type III. The working electrode used in the voltammetry experiments was a modified carbon paste electrode and a platinum wire was used as the counter electrode and reference electrode was Ag/AgCl. The pH was measured at 25 ± 1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. The CHN analysis was performed on a Thermo Finnigan Flash EA112 elemental analyzer (Okehampton, UK). N_2 adsorption surface areas were measured by BET technique using a Micromeritics ASPS 2010 analyzer. IR spectra were recorded on a Bruker IFS-66 FT-IR Spectrophotometer. Low-angle X-ray diffraction patterns were obtained on a Philips-PW 17C diffractometer with Cu K_α radiation. Thermogravimetry and differential scanning calorimetry (TG/DTA) was carried out on a Bahr STA-503 instrument under air atmosphere. The TEM micrograph was recorded by a Philips EM420 transmission electron microscope.

2.3. Preparation of mesoporous carbon

Mesoporous carbon was synthesized according to the recently reported procedure using D-fructose (Fru) as a carbon source [36]. In this approach, 0.25 g of Pluronic F127 and 1.20 g of fructose were dissolved in 10 mL of deionized water and then solution was transferred to a teflon lined sealed steel autoclave and placed at 130 °C for 3 days. Then the dark-brown solid precipitate was obtained and washed with water and ethanol then dried at room temperature. The calcination was performed under nitrogen atmosphere at 550 °C for 6 h. The synthesis of mesoporous carbon was confirmed by X-ray powder diffraction and also nitrogen adsorption analysis.

2.4. Preparation of mercapto-mesoporous carbon

In this approach, in a typical reaction, 1.0 g of mesoporous carbon was suspended in 50 mL toluene, and 3-thiol-propyltriethoxysilane (2.0 mL) was added to the mixture and was refluxed for 48 h under nitrogen atmosphere. Then the black solid was removed from solvent by filtration, washed with methanol and acetone and then dried at room temperature. The synthesis of thiol-functionalized mesoporous carbon was characterized by IR spectroscopy, low-angle X-ray diffraction, transmission electron microscopy, and elemental and thermal analyses. Fig. 1 provides a scheme for the synthesis and application of the sensor. Propose electrochemical reaction of omeprazole on the surface of the modified electrode was shown in Fig. 1.

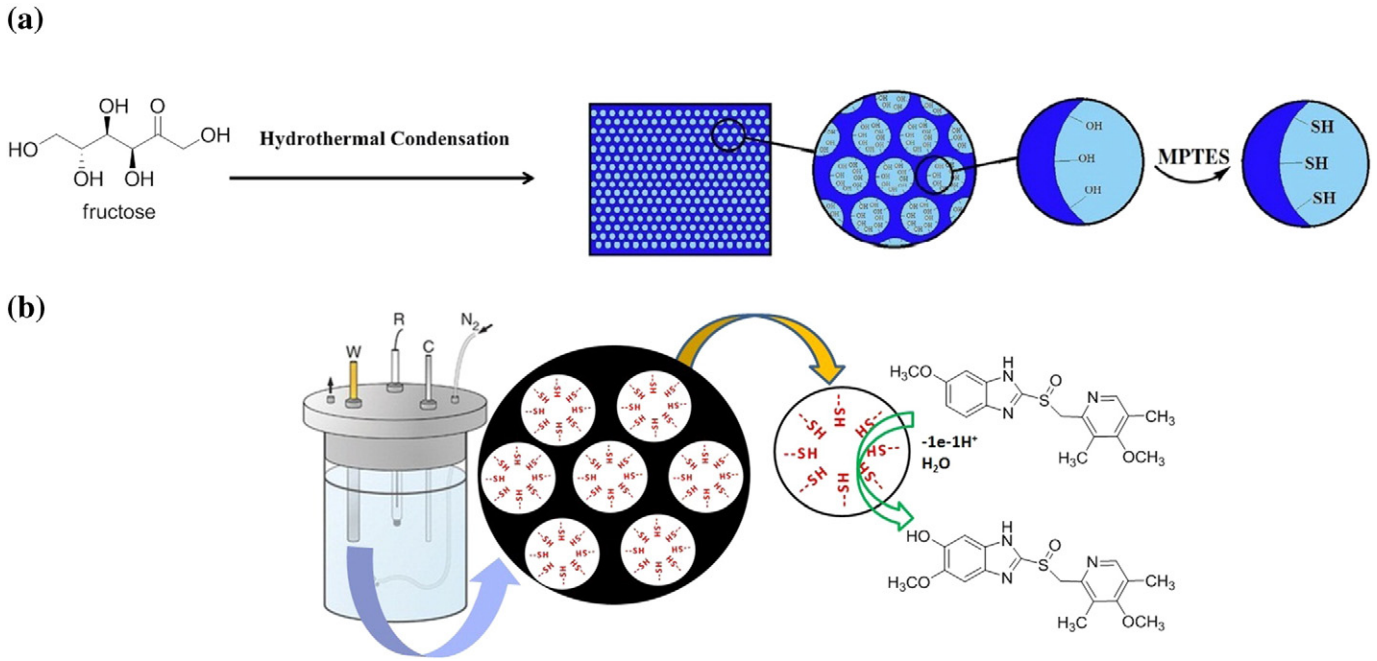

Fig. 1. A scheme for synthesized (a) and application (b) of the novel sensor.