



Selective electrochemical sensor for theophylline based on an electrode modified with imprinted sol–gel film immobilized on carbon nanoparticle layer

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ABSTRACT

A novel electrochemical sensor based on an imprinted hybrid sol–gel film for selective and sensitive determination of theophylline was developed. The imprinted hybrid sol–gel film was prepared by using a new organosilane synthesized as a functional precursor, theophylline as a template and tetraethoxysilane as a matrix forming precursor. The mixture was allowed to hydrolyze, and then spin coated on glassy carbon electrode covered by carbon nanoparticles with sulfonic acid groups that were introduced for immobilization of imprinted sol–gel film and for enhancement of electronic transmission. The morphology and performance of the imprinted film were investigated in detail by scanning electron microscopy, FTIR Spectroscopy, cyclic voltammetry and differential pulse anodic stripping voltammetry. Molecularly imprinted sol–gel was employed to achieve a suitable conformation for electrochemical oxidation of theophylline and also to improve the selectivity of the sensor. The results showed that the imprinted film exhibited selectivity toward theophylline compared to the random sol–gel film prepared in the absence of the template. The imprinted sensor was also successfully employed to detect theophylline in a drug sample.

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1. Introduction

Theophylline (TP) is a widely used drug in treatment of asthma and chronic bronchospasm of adults [1,2]. Levels of TP in plasma below 5–20 $\mu\text{g mL}^{-1}$ range are believed non-therapeutic, while higher levels can cause many undesired side effects and harm to human health. Thus, convenient and reliable methods for detection of TP are of high importance. Up to now, a number of analytical methods, such as gas chromatography–mass spectrometry [3], capillary electrophoresis [4], immunoassay [5], thin layer chromatography [6,7], high-performance liquid chromatography [8,9] and spectrophotometry [10,11] are developed for the determination of TP. However, these methods have some disadvantages such as low sensitivity and poor selectivity, time-consuming pretreatment and expensive protocols. Instead, electrochemical methods are excellent alternative for the determination of TP because of their simple and fast response, high sensitivity, without the time-consuming extraction steps, cost effective and ability of

miniaturization. However, electrochemical methods have a main drawback of TP determination with common electrode materials (e.g., glassy carbon, metals) since its oxidation occurs at high positive potential, thus overlapping with the discharge of the electrolytic solution. To deal with this problem, the electrodes are modified with several materials such as carbon nanotubes, graphene oxide and manganese oxide nanoparticles [12–16].

Carbon materials, such as nanotubes and nanofibers have been widely used for the determination of biologically compounds because of their high surface area, unique electronic and nanostructural properties, high electrical conductivity and good stability [17–20]. In the range of carbon materials, carbon nanoparticles (CNPs) (or chemically surface functionalized carbon black) are well known and offer all the advantages of nanocarbons (reactive surface sites, extremely high surface area, conductivity, adsorption sites, etc.) [21–24].

Molecular imprinting is a powerful approach to design smart electrode materials to mimic molecular recognition by natural receptors. Molecular imprinting is carried out by polymerization of functional monomers and an excess amount of cross-linker in the presence of a target molecule (template). The template molecule is entrapped into the polymer network during the polymerization

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process. After the removal of the template from the cross-linked polymer matrix, a molecular recognition site with appropriate size and chemical functionality is produced to rebind the template. Molecular imprinting has been utilized at several fields [25–27]. Moreover, molecularly imprinted polymers (MIPs) are promising materials being used widely in the design of recognition elements in sensors [28]. There are several methods of forming molecularly imprinted films, including sol–gel [29], electrochemical polymerization [30], in situ polymerization [31] and self-assembly [32]. Among them, imprinted sol–gel has been widely used in the development of imprinted sol–gel sensors [33–39]. The imprinting of hybrid sol–gel materials has great interest in the last few decades due to their unique properties [40–42]. Incorporation of functional organic precursor into inorganic sol–gel matrices has become an attractive means to extend the range, variety and nature of the target molecule that can act as template in molecular imprinting [43–46].

In this work, a new organofunctional silane (CoG–TEICPS) was synthesized by the reaction of Crocein orange G (CoG) with triethoxy(3-isocyanatopropyl)silane (TEICPS). A novel imprinted sol–gel film on glassy carbon electrode coated with carbon nanoparticles containing sulfonic acid groups (CNPs–SO₃H), which was used for immobilization of the sol–gel film with functional precursor on the surface of electrode by covalent binding, was prepared by using CoG–TEICPS and tetraethoxysilane (TEOS) in the presence of TP. Since CoG interacts with TP to form complex in solution, CoG–TEICPS was introduced into sol–gel film to improve binding ability of the electrode for the template molecule.

2. Experimental

2.1. Reagents and solutions

1-Phenylazo-2-naphthol-6-sulfonic acid sodium salt, Crocein orange G (CoG), TP, TEICPS and TEOS were purchased from *Sigma-Aldrich*. Carbon nanoparticles: Emperor 2000 was kindly supplied from Cabot Corporation, Boston, MA. All reagents and solutions used were of analytical grade and used without further purification. The stock solution of TP with $1 \times 10^{-3} \text{ mol L}^{-1}$ was prepared with ultra pure water and stored in a refrigerator at 4 °C. Phosphate buffer solution (PBS) was prepared by using 0.1 mol L^{-1} of KH₂PO₄–K₂HPO₄, and adjusting the pH with the solutions of H₃PO₄ and KOH. All aqueous solutions were prepared using ultra pure water from a Millipore Milli-Q system (system resistivity equal to 18 MΩ cm).

2.2. Apparatus

Electrochemical experiments were performed using a Versastat 3 potentiostat/galvanostat. A conventional three-electrode system was employed with a bare GCE with 2 mm diameter (PAR-G0229) as a working electrode, an Ag/AgCl/3 M KCl as a reference (PAR-K0265) electrode, and a platinum wire as a counter electrode (PAR-K0266). Oxygen was removed by purging with high purity nitrogen for 10 min, and nitrogen atmosphere was kept over the solution during measurement. All of the pH values were measured with a VWR 730P pH meter. Attenuated total reflectance-infrared (ATR-FTIR) spectra of the samples were recorded on a Perkin Elmer Spectrum v5.0.1 FTIR spectrometer. UV–vis spectra of samples were obtained with a VWR UV-1600 PC Spectrophotometer. The surface morphologies of the imprinted and non-imprinted sol–gel films were evaluated by scanning electron microscope (LEO Supra VP35 FE-SEM) images. Spin coating of the film was achieved with specialty coating systems (SCS Spincoat G3-8).

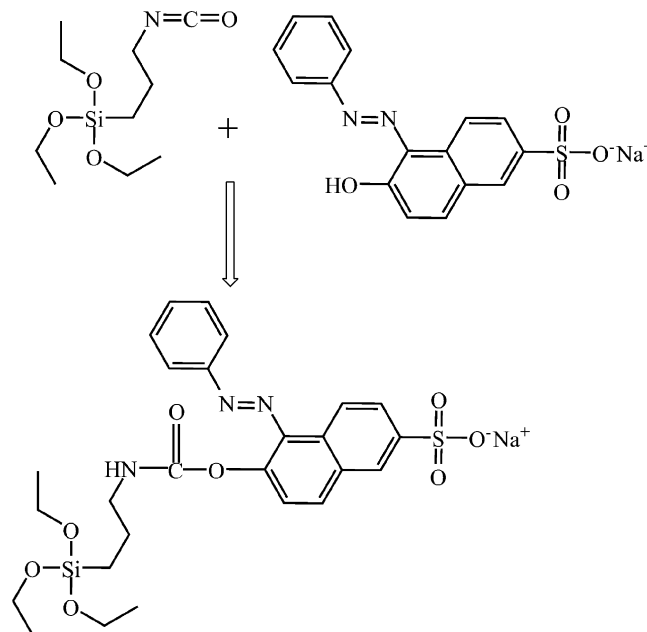


Fig. 1. Scheme of the synthesis process of CoG–TEICPS.

2.3. Synthesis of CoG–TEICPS

CoG–TEICPS was prepared as follows: CoG (145 mg, 0.414 mmol) was dissolved in anhydrous tetrahydrofuran and put into the three-necked glass flask. TEICPS (102.4 μL, 0.414 mmol) was added drop by drop for about one hour under nitrogen atmosphere and then after addition of 50 μL of triethylamine, the obtained dark orange solution was stirred for 24 h under reflux. After reaction, the solvent was removed by evaporation and the residue was directly purified by flash column chromatography (silica gel, CHCl₃/CH₃OH) to provide CoG–TEICPS as a red compound (Fig. 1).

2.4. Preparation of imprinted sol

A hybrid sol was prepared by mixing 0.6 mL of TEOS, 0.6 mL of ethanol, 47 mg of (0.135 mmol) CoG–TEICPS, 0.1 mL of concentrated HCl and 0.1 mL of H₂O. The sol became clear and transparent after persistently stirring for about 2 h. Then, 0.5 mL of the sol was mixed with the template molecule, TP (12.1 mg, 0.0675 mmol), to prepare the imprinted sol. Remaining sol without TP was used for non-imprinted, random films (NIPs).

2.5. Electrode preparation and procedures

2.5.1. Fabrication of CNPs–SO₃H modified GCE (CNPs–SO₃H/GCE)

Prior to modification, the surface of GCE was polished with 1.0, 0.3 and 0.05 μm alumina slurry, respectively by using a polishing cloth to produce a mirror-like surface. Then, the electrode was rinsed with distilled water, sonicated for three minutes in water and ethanol mixture, and dried in the air. 0.2 mg of CNPs–SO₃H was dispersed in 5 mL of dimethylformamide (DMF) in ultrasonic bath to obtain a black solution. The 10 μL of this solution was dropped on the polished GCE surface and spun at 3000 rpm for 30 s. Then, DMF was evaporated in the air to obtain a CNPs–SO₃H modified GCE.

2.5.2. Fabrication of imprinted sol–gel sensor electrode (MIP/CNPs–SO₃H/GCE)

To fabricate MIP/CNPs–SO₃H/GCE sensor electrode, MIP sol was spin coated by placing of 30 μL on CNPs–SO₃H/GCE and by

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