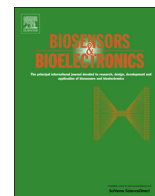




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# Caffeine electrochemical sensor using imprinted film as recognition element based on polypyrrole, sol-gel, and gold nanoparticles hybrid nanocomposite modified pencil graphite electrode



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## ABSTRACT

In the present study, a novel sensitive and selective nanocomposite imprinted electrochemical sensor for the indirect determination of caffeine has been prepared. The imprinted sensor was fabricated on the surface of pencil graphite electrode (PGE) via one-step electropolymerization of the imprinted polymer composed of conductive polymer, sol-gel, gold nanoparticles (AuNPs), and caffeine. Due to such combination like the thin film of molecularly imprinted polymer (MIP) with specific binding sites, the sensor responded quickly to caffeine. AuNPs were introduced for the enhancement of electrical response by facilitating charge transfer processes of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  which was used as an electrochemical active probe. The fabrication process of the sensor was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Several important parameters controlling the performance of the sensor were investigated and optimized. The imprinted sensor has the advantages of high porous surface structure, inexpensive, disposable, excellent stability, good reproducibility and repeatability. The linear ranges of the MIP sensor were in the range from 2.0 to 50.0 and 50.0 to 1000.0  $\text{nmol L}^{-1}$ , with the limit of detection (LOD) of 0.9  $\text{nmol L}^{-1}$  ( $S/N=3$ ). Furthermore, the proposed method was successfully intended for the determination of caffeine in real samples (urine, plasma, tablet, green tea, energy and soda drink).

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## 1. Introduction

Caffeine (1, 3, 7-trimethylxanthine) is an active alkaloid and a stimulant drug widely found in the human diet. We consume caffeine daily in coffee, tea, chocolate, energy or soft drinks, and in many painkillers and antimigraine drugs. Caffeine acts as a central nervous system stimulant, cardiovascular system stimulant, and alleviation of migraine. However, high amounts of caffeine in the body may cause many undesired physical and mental conditions (Gupta et al., 2013; Peri-Okonny et al., 2005; Reissig et al., 2009). Therefore, the investigation and determination of caffeine in beverage, pharmaceutical, and biological samples is very important. Various analytical methods have been reported for the determination of caffeine, including chromatography (Chen et al., 2010a; Hadad et al., 2012; Rajabi Khorrami and Rashidpur, 2012), spectrometry (del Campo et al., 2010; Jafari et al., 2011), FT-Raman (Armenta et al., 2005), and electrochemical sensors (Gupta et al., 2013; Santos et al., 2012; Sun et al., 2011). Despite these techniques

have high sensitivity and accuracy, some factors such as expensive instrumentation, time consuming, highly skilled techniques and complicated procedures restricted their application. Electrochemical methods, especially electrochemical molecularly imprinted polymer (MIP) based sensors, have attracted more attention in recent years due to their simplicity, high sensitivity and selectivity, good stability, low cost instrumentation, fast response and real time detection (Afkhani et al., 2013; Prasad et al., 2010; Xue et al., 2013).

The MIP technique has been demonstrated as a powerful technique in designing and synthesizing some artificial receptor molecules for the mimicking of biological functions usable in analytical chemistry. MIPs have been extensively utilized in various fields including sensors, separations, sample pretreatment, and catalysis (Chen et al., 2010b; Cirillo et al., 2011; Huang et al., 2011; Kirsch et al., 2009). Traditional MIPs have encountered many limitations including incomplete template removal, poor site accessibility, slow interaction kinetics, heterogeneous nature of the binding sites, and irregularity in the shape of materials (which relied upon the bulk polymerization approach) (Liu et al., 2012; Zeng et al., 2013). To overcome these problems, the use of surface MIPs was suggested (Jing et al., 2010; Lu et al., 2007). In comparison with conventional methods for MIPs preparation, electropolymerization offers a simple, reproducible,

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convenient and friendly to environment way for the deposition of thin recognition film directly on the support surface of any size and shape (Kan et al., 2012; Liu et al., 2012).

Conducting polymers comprise a group of compounds and materials with very specific properties, which have permeated many fields of electrochemical research. Polypyrrole (Ppy) and its derivatives have become one of the most widely used conductive polymers in the design of sensors and biosensors due to their significant electrical conductivity, good biocompatibility, and its stable films can easily be deposited electrochemically (Kan et al., 2012; Mehdinia et al., 2013). The interaction between the conductive polymers and the other constituents resulted in a novel material that can be used for specific applications.

In addition to conductive polymers, the sol-gel technology has also been applied to improve the performance of MIPs on the sensor surface. The sol-gel technology provides a simple way to prepare three dimensional silicate networks with desirable sorptive properties, through efficient incorporation of organic components into the inorganic polymeric structure. The sol-gel based MIPs possess numerous significant advantages over conventional MIPs, such as simple fabrication process, mild thermal reaction condition, physical rigidity, chemical inertness of the matrix, and matrix porosity due to highly cross-linked structure (Mao et al., 2012; Yang et al., 2013). However, the electrical insulation property of sol-gel based coatings is clearly an undesirable property and poses severe limitations on the efficiency of the signal transduction process. Due to the electrically insulating layer of sol-gel MIP based systems; a direct path for the conduction of electrons from the binding sites to the electrode surface is required. In order to overcome the limitations of rebinding capacity and conductivity, the most effective way was the use of conducting nanomaterials. Metal nanoparticles have attracted widespread attention in their utilization for enhancing the sensitivity of the electrochemical detection. Among all kinds of metal nanoparticles, gold nanoparticles (AuNPs) have been extensively used in fabrication of different kinds of sensors due to their unique structure and fascinating properties such as high effective surface area, strong adsorption ability, good biocompatibility and conductivity. The nanocomposite of AuNPs doped MIPs can be easily constructed by some strategies including direct electrostatic assembly, covalent linking, polymer entrapment, co-mixing, and electrodeposition methods (Guo and Dong, 2009; Li et al., 2013; Yu et al., 2012).

The incorporation of AuNPs, conductive polymers, and sol-gel technology allows preparation of new nanocomposite that can efficiently combine the advantages of all materials. The advantages of using this nanocomposite MIP sensor compared to other sensors (i.e. electrochemical sensors consisting of layer by layer modified electrode) are ease of preparation (one-step electropolymerization), low cost, more porous surface structure, higher recognition capacity, higher functional groups, excellent selectivity and sensitivity. In addition, it is possible to design the MIP film properties and polarity through proper selection of the sol-gel precursor and conductive polymer derivatives.

In the present paper, we propose a simple approach to improve the conduction of electrons from sol-gel MIPs to the electrode surface with the entrapment of conductive polymers and metal nanoparticles within sol-gel networks. To the best of our knowledge, this is the first work describing synthesis and use of a conducting polymer, sol-gel, and AuNPs hybrid nanocomposite as a MIP based electrochemical sensor (nanocomposite MIP/PGE). The experimental parameters that affect the performance of the nanocomposite MIP sensor were investigated and optimized. The nanocomposite MIP sensor was evaluated to confirm its electrochemical properties (selectivity, conductivity, stability, linearity, repeatability and reproducibility). Furthermore, the developed imprinted sensor was applied for the analysis of the caffeine in real samples.

## 2. Experimental

### 2.1. Materials

Tetraethoxysilane (TEOS), phenyltriethoxysilane (PTEOS), sodium dodecyl sulfate (SDS), trifluoroacetic acid (TFA), hydrogen tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), and caffeine were purchased from Merck (Darmstadt, Germany). All other solvents and salts used in this study were of analytical grade and were obtained from Merck (Darmstadt, Germany). Ethanol was prepared from Bidestan Co. (Qazvin, Iran). Pyrrole (Merck, Darmstadt, Germany) was distilled and stored in a dark bottle in a refrigerator before use.

Caffeine stock solution was prepared and stored at 4 °C prior to use. More diluted working solutions used in further studies were prepared daily by diluting different amounts of the intermediate standard solution with phosphate buffer (pH 4.0) to the required concentrations.

### 2.2. Instrumentation

The electrochemical measurements were performed with a Potentiostat-Galvanostat  $\mu$ -AutoLab (Echo Chemie, B.V., Netherlands, NOVA software). A three-electrode system consisted of an Ag/AgCl reference electrode, a platinum rod auxiliary electrode, and a nanocomposite MIP/PGE as the working electrode was used. Autolab system (PGSTAT 12, Eco Chemie B.V., Utrecht, Netherlands) was applied for the electrochemical impedance spectroscopic measurements. The system was performed on a PC by GPES and FRA 4.9 software.

A mechanical pencil was used as a holder for graphite leads (Rotring, 2B, 0.7 mm diameter, Germany). Electrical contact with the lead was obtained by soldering a metal wire to the metal part. Metrohm pH meter (Model 827) with a glass electrode (Corning) was used to adjust the solution pH. An atomic force microscope (BRUKER, Germany) was used to investigate AuNPs electrodeposited into the nanocomposite MIP. The scanning electron microscopy images (SEM) were obtained using a Philips XL30 SEM instrument.

### 2.3. Preparation of nanocomposite MIP/PGE

The surface of the pencil lead was first pretreated by applying potential +1.40 V for 300 s in 0.50 mol L<sup>-1</sup> acetate buffer (pH 4.8) containing 0.02 mol L<sup>-1</sup> sodium chloride.

A typical procedure for preparing nanocomposite film is described as follows. The sol solution was prepared using 75  $\mu$ L of PTEOS, 75  $\mu$ L of TEOS, 700  $\mu$ L of water, 1100  $\mu$ L of ethanol, 10  $\mu$ L of TFA, and caffeine (2.5 mmol L<sup>-1</sup>) in a vial. The mixture was stirred for 2 h at room temperature. Immediately following, 50  $\mu$ L of pyrrole solution (final concentration of 25.0 mmol L<sup>-1</sup>), 5.0 mg of SDS (as the counter ion), and 50  $\mu$ L of 0.01%  $\text{HAuCl}_4$  solution (final concentration of  $2.5 \times 10^{-4}\%$ ) were added to the mixture. The resulting polymerization solution was sonicated for 10 min. Then, the pretreated electrode was immersed into the polymerization solution. The nanocomposite MIP film was prepared by electrodeposition using CV in the potential range of -0.80 and +0.60 V (versus Ag/AgCl) during five cycles. After electrodeposition the modified electrode was dried at room temperature for 2 h. The doped caffeine was extracted from the imprinted film by immersion in acetic acid (50% V/V) solution with stirring magnetically for 20 min.

For the comparison purpose, a sol-gel/AuNPs nanocomposite and a ppy/sol-gel/AuNPs layer-by-layer MIP electrode were fabricated by the method given in Supplemental information. As a reference electrode, the non-imprinted polymer (NIP) electrode

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