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Using gold nanostars modified pencil graphite electrode as a novel substrate for design a sensitive and selective Dopamine aptasensor

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ABSTRACT

For the first time, gold nanostars (GNS) were applied for electrostatic and covalent immobilizing a thiol modified Dopamine aptamer on the pencil graphite electrode and signal amplification. Dopamine aptamer was immobilized on the gold nanostars through electrostatic interaction between negatively charged phosphate groups of aptamer and positively charged gold nanostars and Au—S well known covalent interaction. In the presence of Dopamine in the test solution, the charge transfer resistance (R_{CT}) on the electrode surface increased with the increase of the Dopamine concentration due to specific interaction between Dopamine aptamer and Dopamine molecules, which made a barrier for electrons and inhibited the electron-transfer. So, the proposed approach showed a high sensitivity and a wide linearity to Dopamine in the range from 1.0 (±0.1) to 100.0 (±0.3) ng L^{-1} (ppt) with detection and quantification limits of 0.29 (±0.10) and 0.90 (±0.08) ng L^{-1} (ppt), respectively. Finally, the sensor was successfully used for determination of Dopamine in biological (human blood plasma and urine) samples. The results open up the path for manufacturing cost effective aptasensors for other biomedical applications.

1. Introduction

Catecholamines (include compounds with a di-hydroxy phenyl group and an amine group) represent a group of biogenic amines, among which epinephrine, norepinephrine, Dopamine and L-dopa act as neurotransmitters in the function of brain and nerve signal transduction [1].

The measurement trace concentration of Dopamine in biological fluids has an essential role in the diagnosis of diseases and medicine controlling because many diseases are related to the change of Dopamine concentration. In recent years, many methods have been reported for determination of Dopamine like neurotransmitters in pharmaceutical preparations and biological samples, such as electrochemistry [2], chemiluminescence [3], spectrofluorimetry [4], high performance liquid chromatography (HPLC) with different detectors [5], and mass spectrometry [6]. Many current techniques for neurotransmitters detection, such as capillary electrophoresis, liquid chromatography and mass spectrometry, despite their good sensitivity, require expensive and sophisticated instrumentation or complicated sample preparation and time consuming processes. Thus, the development of a sensitive, fast and practical method for neurotransmitters detection still remains a great challenge.

Electrochemical impedance spectroscopy (EIS) is a rapidly developing electrochemical technique [7]. Electrochemical biosensors based on impedance technique have proved to be a promising method for drug detection [8,9] because of their portability, rapidity, sensitivity, low cost, ease of miniaturization, and label-free operation [10].

In the past few years, different aptasensors for Dopamine detection have been reported. Unfortunately, most of these aptasensors suffer poor sensitivity and selectivity, complicated sensor structure and weak analytical performance [11,12].

In order to enhance the sensitivity and selectivity of aptasensors, a variety of materials have been employed for the electrode modification. Recently, researchers have been synthesized gold nanostars (GNS) using seeded [13–15] and seedless [16–19] growth methods. The strong near-infrared (NIR) absorptions of the GNS shows potential applications of GNS in SERS [20], catalysis [20], and especially in photothermal therapy [21]. But there is no report for use of gold nanostars in modification of electrode surface and constructing electrochemical sensors. The aim of this paper was designing a simple, sensitive and selective Dopamine EIS aptasensor using gold nanostars as a signal amplifier and a suitable template for aptamer immobilization. Our proposed aptasensor has great analytical performance toward previously reported Dopamine assays. Furthermore, simple preparation and very good stability, repeatability and regeneration ability of our electrode, might bring further insight into manufacturing the other new, sensitive, and inexpensive drug aptasensors. In this work, we used gold nanostars modified pencil

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graphite electrode as a novel substrate for ultra-trace Dopamine determination. Our result showed gold nanostars can increase pencil graphite electrode surface and amount of the immobilized Dopamine aptamer. Indeed, the gold nanostars with positive charge on their surface electrostatically interact with negative charge of phosphate group of Dopamine aptamer and covalently interact with thiol group of Dopamine aptamer through well known Au—S bond. The covalent and electrostatic interactions are two main strategy that have been used in the successful immobilization of DNA and aptamer in many reports [9]. Thereupon, Dopamine aptamer can be tightly grafted to the modified pencile graphite electrode. In the presence of Dopamine, the increase in the charge transfer resistance (R_{CT}) at the modified pencil graphite electrode was observed because complex formation between aptamer and Dopamine which blocked the electron transfer process at the electrode surface because of the electrostatic repulse of $[Fe(CN)_6]^{3-/4-}$ with the immobilized aptamer. When the Dopamine concentration was increased in the solution, the ΔR_{CT} (difference between charge transfer resistance of modified electrode before and after incubation with Dopamine) increased, and the values of ΔR_{CT} were linear with Dopamine concentrations in the solution. Scheme 1 illustrates various steps of fabrication of aptamer based electrochemical sensor. The proposed aptasensor was successfully used for Dopamine determination in the complex biological matrixes, and would become a simple and powerful tool for bio-analysis and clinical application.

2. Experimental

2.1. Materials

Dopamine was prepared from the Pharma Shimi Pharmaceutical Company (Iran). Cetyl tri-methyl ammonium bromide (CTAB), hydrogen tetra-choloroaurate ($HAuCl_4 \cdot 3H_2O$), ascorbic acid ($C_6H_8O_6$), tri-sodium citrate ($Na_3C_6H_5O_6$), potassium mono-hydrogen phosphate (K_2HPO_4), potassium di-hydrogen phosphate (KH_2PO_4), $K_3Fe(CN)_6$, and $K_4Fe(CN)_6$ were obtained from the Merck Company (Germany). Mercapto-hexanol (MCH) was procured from the Sigma-Aldrich Company (USA) and athiol modified Dopamine aptamer was acquired from the Aminsan Company (Iran) with the following sequence: 5′-S-H-GTC TCT GTG TGC GCC AGA GAA CAC TGG GGC AGA TAT GGG CCA GCA CAG AAT GAG GCC C-3′.

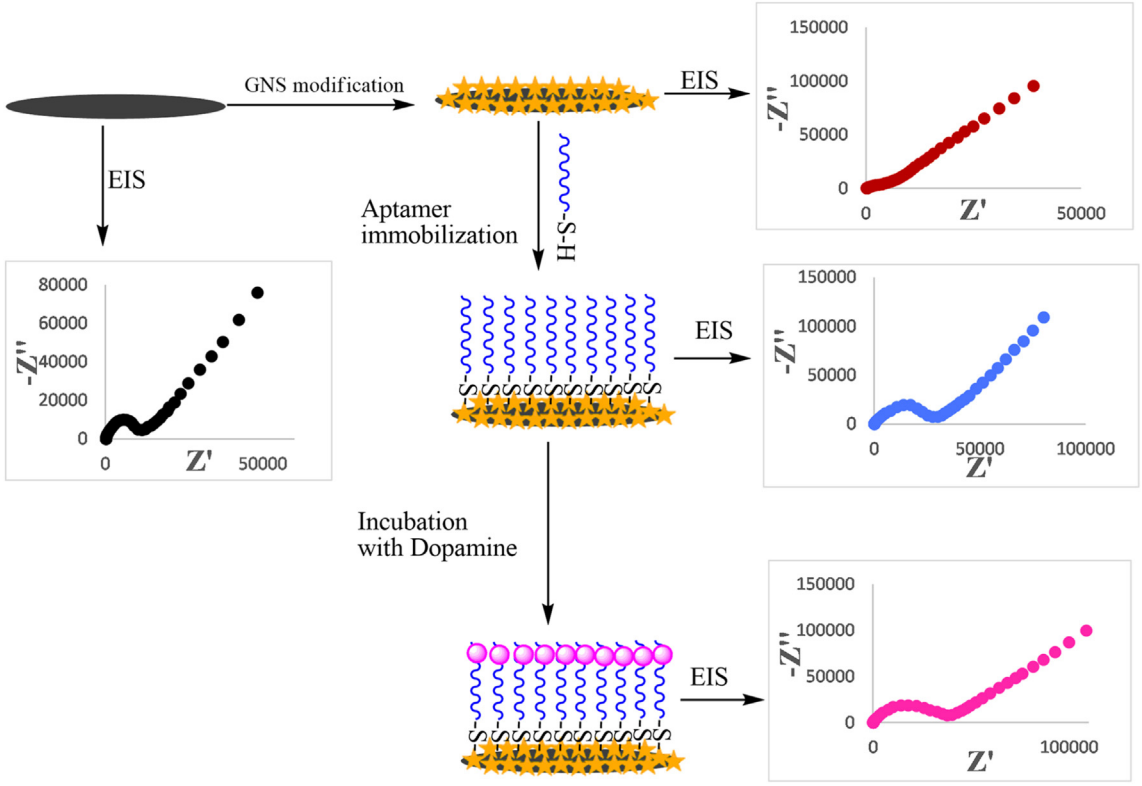
Dopamine aptamer was dissolved in 0.1 mol L^{-1} phosphate buffer solutions (PBS, pH 7.4) and was kept in refrigerator at 4 °C. All analytical reagent grade chemicals and distilled water were used for preparing all aqueous solutions.

2.2. Instruments

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were carried out with an Autolab 302 N electrochemical workstation (Metrohm, The Netherlands). A three electrode system, composed of a platinum electrode as auxiliary (Azar electrode, Iran), an Ag/AgCl (saturated KCl) as a reference electrode (Azar electrode, Iran), and an unmodified/modified pencil graphite electrode (PGE) as working electrode was used in the experiments. The morphologies of the synthesized and modified gold nanostars were characterized with a JEM 1200 EXII transmission electron microscope (JOEL company-USA) and Scanning electron microscopy (SEM) measurements were performed by a TESCAN scanning electron microscope (Czech).

2.3. Preparation of gold nanostars

Gold nanostars (GNS) were synthesized according to seed-mediated growth protocol [22]. Gold seeds were achieved by adding freshly prepared $NaBH_4$ (60 mL, 0.1 mol L^{-1}) to a 10 mL solution of tri-sodium citrate (1 mmol L^{-1}) capped $HAuCl_4.3H_2O$ (0.2 mmol L^{-1}) under stirring,



Scheme 1. Schematic presentation of different steps of aptasensor construction.