Talanta 159 (2016) 307–316

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

An electrochemical dopamine aptasensor incorporating silver nanoparticle, functionalized carbon nanotubes and graphene oxide for signal amplification

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ARTICLE INFO

Article history:
Received 15 January 2016
Received in revised form
21 May 2016
Accepted 24 May 2016
Available online 24 May 2016

Keywords:
Aptasensor
Graphene oxide
Chitosan
Silver nanoparticle
Dopamine

ABSTRACT

In this work, immobilization of a dopamine (DA) aptamer was performed at the surface of an amino functionalized silver nanoparticle-carbon nanotube graphene oxide (AgNPs/CNTs/GO) nanocomposite. A 58-mer DA-aptamer was immobilized through the formation of phosphoramidate bonds between the amino group of chitosan and the phosphate group of the aptamer at the 5′ end. An AgNPs/CNTs/GO nanocomposite was employed as a highly catalytic label for electrochemical detection of DA based on electrocatalytic activity of the nanocomposite toward hydrogen peroxide (H_2O_2). Interaction of DA with the aptamer caused conformational changes of the aptamer which, in turn, decreased H_2O_2 oxidation and reduction peak currents. On the other hand, the presumed folding of the DA–aptamer complexes on the sensing interface inhibited the electrocatalytic activity of AgNPs/CNTs/GO toward H_2O_2. Sensitive quantitative detection of DA was carried out by monitoring the decrease of differential pulse voltammetric (DPV) responses of AgNPs/CNTs/GO nanocomposite toward H_2O_2 oxidation. The DPV signal linearly decreased with increased concentration of DA from 3 to 110 nmol L^{-1} with a detection limit of 700 ± 19.23 pmol L^{-1}. Simple preparation, low operation cost, speed and validity are the decisive factors of this method motivating its application to biosensing investigation.

1. Introduction

As is well known, aptamers are short synthetic single-stranded DNA or RNA oligonucleotides that are selected through SELEX (systematic evolution of ligands by exponential enrichment) processes from a random sequence bank [1,2]. Aptasensors with high affinity and specificity towards a wide variety of target molecules including proteins, enzymes, antigens, antibiotics, toxins, pharmaceutical drugs and even viruses and whole cells [3,4] have been utilized as powerful molecular recognition tools, not only in drug design and delivery, but also in analytical bioassay [5]. Excellent binding affinity and significant selectivity of aptamers make them as attractive as antibodies. However, DNA aptamers have some key advantages compared with antibodies, such as a cheap synthesis, a comparatively smaller size, an in vitro selection process, an increased resistance to degradation, and reversible denaturation. Thus, they have been used as alternatives to antibodies in various fields for different usages [6,7].

A binding event between aptamer and specific target can be transduced via colorimetry [8], fluorimetry [9], surface plasmon resonance (SPR) [10], quartz crystal microbalance (QCM) and electrochemical techniques [11]. The significant advantages of electrochemical aptasensors are their fast response, high sensitivity, simplicity, simple operation, reusability, and relatively low cost. These features make them promising sensors for the detection of various small molecules and proteins [12–14].

Dopamine is an organic chemical of the catecholamine and phenethylamine families, and is part of the hormonal, cardiovascular and central nervous systems [15–17]. Many biological functions such as motivation, emotion, endocrine regulation, and locomotion are controlled by dopamine. Furthermore, diseases such as Parkinson, schizophrenia and Huntington's chorea are associated with extreme abnormalities of dopamine levels [18–20]. Here, a label-free aptamer assay as a sensitive and selective biorecognizer for detection of DA is reported.

The unique catalytical, electrical, magnetic, optical, and chemical properties of nanostructure material including

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http://dx.doi.org/10.1016/j.talanta.2016.05.060
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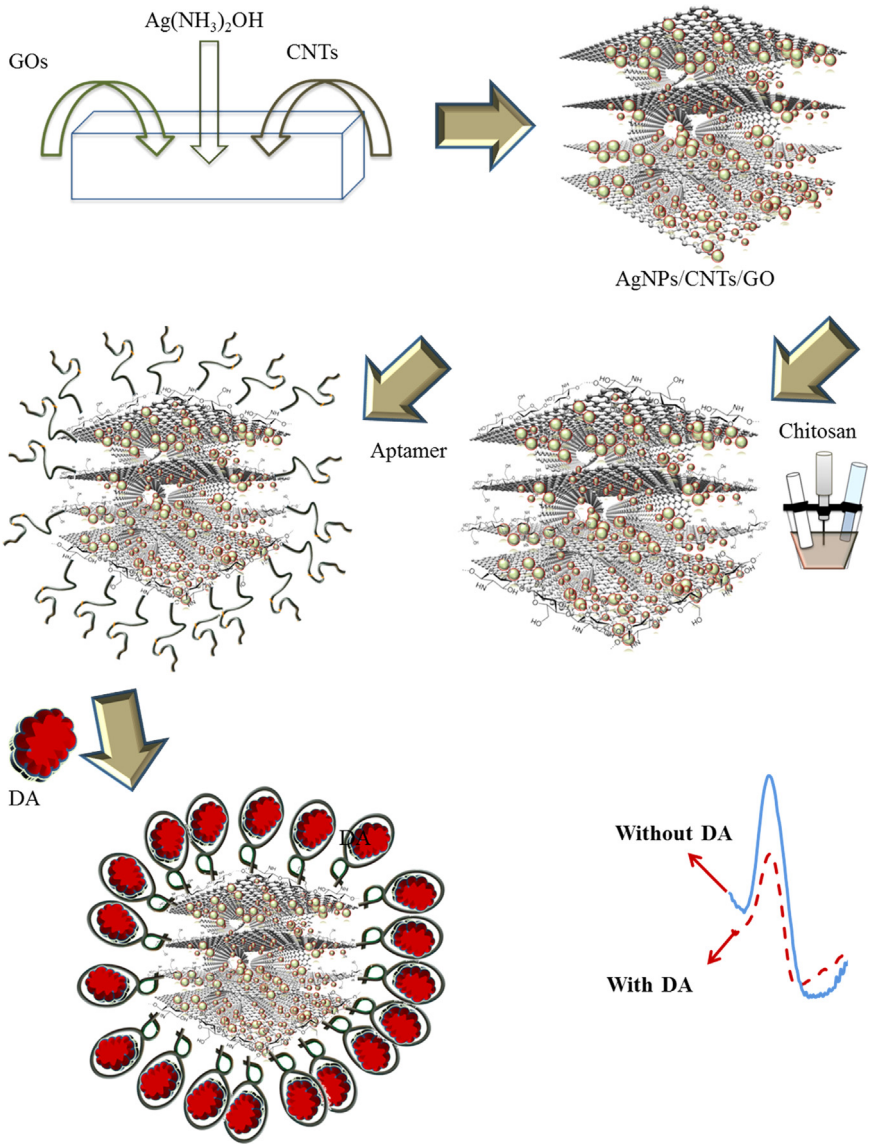

Fig. 1. Schematic representation of different steps of aptasensor fabrication.

nanocomposites, nanoparticles, and nanomaterials have a significant influence on other fields such as nanoelectronics, photonics, biology, and medicine [21]. Furthermore, nanomaterials can be attached to biomolecules such as antibodies, antigens, and nucleic acids as active units in bioanalytical systems. Thus, biomaterial hybrid films based on nanomaterials are broadly used in different biosensing applications [22,23]. In order to improve electronic and thermal conductivity of graphene nanosheets, graphene-based composite nanomaterials were prepared via molecular level dispersion of graphene in polymers [24]. Recently, graphene-based nanocomposites have been used to support metal nanoparticles (NPs) such as PtNPs and AuNPs [25,26]. Metal nanoparticle-graphene nanocomposites have shown promise in numerous fields such as chemical sensors, energy storage, catalysis, and hydrogen storage [25]. Moreover, adhesion of metal nanoparticles to graphene inhibits aggregation of the graphene nanosheets in the dry state. Also, metal nanoparticles act as spacers and increase the distance between the graphene nanosheets, thereby making both faces of graphene accessible [26]. A simple synthetic way for high density attachment of silver nanoparticle onto the sides of graphene oxide (GO) and carbon nanotube (CNTs) by a simple method without reducing agent has been recently reported [27].

In this work, a one-step method for preparation of AgNPs/CNTs/GO was carried out, and the nanocomposite used for immobilization of DA-aptamer. The aptasensor was fabricated based on phosphoramidate attachment between trapped chitosan in the nanocomposite and the phosphate group of the aptamer at the 5′ end. Silver nanoparticles in the AgNPs/CNTs/GO nanocomposite were used as catalytic labels for the oxidation and reduction of H_2O_2. Quantitative detection of DA was carried out by monitoring the differences of the DPV response of the modified electrode toward H_2O_2 oxidation before and after adding different concentrations of DA. In the presence of DA, due to formation of DA–aptamer complexes at the sensing interface, the electrocatalytic activity of AgNPs toward H_2O_2 oxidation was inhibited.

2. Experimental

2.1. Chemicals

Multiwall carbon nanotubes with purity 95% (10–20 nm diameters) and 1 μm length were obtained from Nanolab (Brighton,