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Research Paper

An electrochemical adenine sensor employing enhanced three-dimensional conductivity and molecularly imprinted sites of Au NPs bridged poly(3-thiophene acetic acid)

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ABSTRACT

An electrochemical strategy for adenine detection was described. In order to generate a 3D net-work composite film, gold nanoparticles (Au NPs) capped with 3-thiophene acetic acid (3-TAA) were used to couple with molecular imprinting technique (MIT). In the presence of the 3-TAA capping Au NPs (Au NPs-T), the electrode-surface-tethered 3-TAAs were polymerized to form a homogeneous conductive material immobilized into the electrode. Through this sensor fabrication, Au NPs-T associating with the Au electrode resulted in enhanced sensitivity and MIT contributed to the specificity.

1. Introduction

As one of the four important bases which present in DNA, adenine has a variety of roles in biochemistry including cellular respiration, cerebral circulation, enzymatic reactions as cofactors, energy transduction and cell signaling. The abnormal variations of adenine concentration in organism suggest the deficiency and mutation of the immunity system and may indicate the presence of various diseases [1–3]. Demands for robust analysis of adenine have led diverse researches to focus on the development of tailor-made analytical chemical sensors with enhanced sensitivity and selectivity. Electrochemical imprinted sensors, based on molecular imprinted technique, have become attractive sensing tools with inherent simplicity, miniaturization, tailorability, robustness, less-expensive and multiple choices of templates [4].

Imprinting electropolymerization, that is generating selective binding sites for analyte on the surface of electrode [5], paves a way for directly immobilizing polymer film on the transducer surface. With the possibility to control the molecular imprinted film thickness through the amount of charge passed during electropolymerization [6], the performance of resulting film could be tuned in optimization.

Among the extensive possibilities offered by chemistry, the coupling of gold nanoparticles (Au NPs) with molecular imprinted polymer (MIP) has been used in generating interconnection networks for the design of Au NPs/MIP sensors. With quantum size effect which leads to discrete electro transition energy levels, Au NPs show excellent conductivity [7], unique electronic and catalytic properties [8], adding new dimensions to the area of electrochemical sensors. Compared to insulating vinylic polymers modified Au NPs, the conducting polymers modified Au NPs which base on conducting polymers such as aromatic thiols and thiophene, were constructed into three-dimensional Au NPs matrixes with further increasing conductivity [9–12].

With unique advantages, 3-thiophene acetic acid (3-TAA) was taken into account in meeting the dual need both on conductivity and specific interaction to Au NPs. One peculiarity is that 3-TAA could stabilize Au NPs with fully conjugated groups in three dimensions as thiophene derivative, which resulted in several orders of magnitude higher conductivity than unlinked NPs or networks consisting of a monolayer of aliphatic thiols-capped Au NPs [13,14]. Besides, attributed to a distinct affinity toward gold, sulfur-containing molecules could absorb on the surface of Au without reducing the adsorbate and oxidizing the gold substrate [15]. As a result, the 3-TAA layers were able to self-assemble on gold nanoparticles which could control the electrostatic nature of the interface of individual nanostructures, resulting in the ability to form large assemblies [16,17]. More than that, carboxylic group of 3-TAA could interact with the amino group of template

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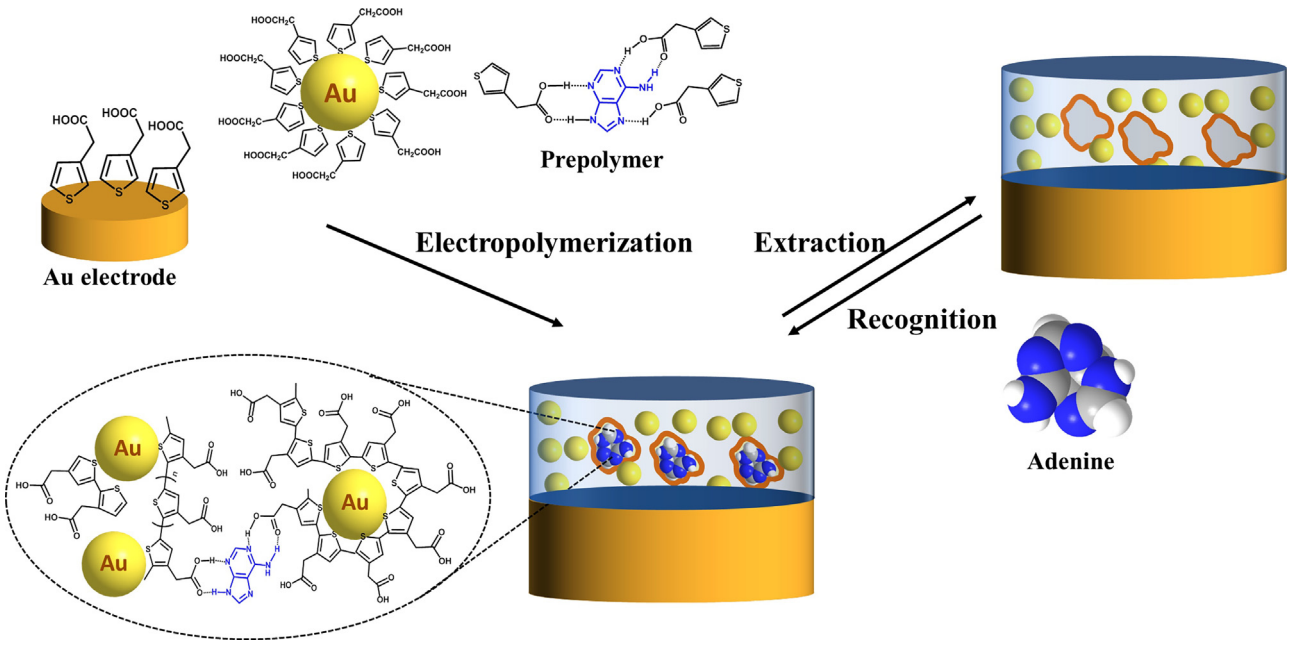

Fig. 1. The scheme of fabrication sensor based on molecularly imprinted composite.

molecule instead of being involved into the polymerization step [18]. Consequently, the conductive hetero 3D net-work film was implemented via electropolymerization of thiophene-capped gold nanoparticles (Au NPs-T) on the Au electrode. Au NPs were embedded in π-conjugated matrixes, leading to a conductive roughened array.

Previous studies have showed that the incorporation of gold nanoparticle with thiophene in electrochemical sensing could be realized through eletrodeposition of gold nanoparticles followed by electropolymerization of monomer onto electrode [19]. In this case, the Au NPs were covered by polymer layer instead of distributed along the polymer film uniformly [20]. In the present study, a highly cross-linked film was generated via thiophene-capped Au NPs, exhibiting superior conductivity and rough surface with enormous recognition sites.

Herein, we devised an innovative electrochemical sensor based on 3-thiophene acetic acid and Au NPs utilizing cyclic voltammetry (CV). It is a hybrid system coupling MIPs with Au NPs-T (MIP/Au NPs-T), in which 3-TAA both as functional monomer in the polymerizing procedure and capping agent to prevent particle aggregation, the preparative procedure is illustrated in Fig. 1. As cross-linker, Au NPs were involved in constructing a three-dimensional network film, with inherent remarkable conductivity which was attributed to the improving interparticle charge transfer [13]. The enhanced performance for adenine detection of the MIP/Au NPs-T electrode may contribute to two primary effects: (1) the conductivity of this hybrid system was significantly improved in the presence of gold nanoparticles embedded into the π-conjugated polymers [21], (2) the selectivity of the analysis was successfully designed via the electrochemical imprinting procedure. The sensitivity and selectivity of the MIP/Au NPs-T film towards adenine were determined using the differential pulse voltammetry (DPV) technique.

2. Experimental section

2.1. Reagents and materials

Adenine and tetrabutylammonium perchlorate were bought from Aladdin Company; thiophene-3-acetic Acid (TAA) was purchased from Tokyo Chemical Industry Co. (Company) (Shanghai, China); chloroauric acid hydrate ($HAuCl_4{\cdot}xH_2O$) was bought from Adamas Reagent Company; sodium borohydride ($NaBH_4$), ethanol, dimethyl sulfoxide (DMSO), acetonitrile (ACN), sulfuric acid (H_2SO_4), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$), hydrogen peroxide (H_2O_2) 30% were obtained from Chemical Reagent Co. (Chongqing, China). The phosphate buffer solution (PBS) was prepared with 0.1 M NaH_2PO_4, and its pH was adjusted with 0.1 M NaH_2PO_4. Deionized water is used throughout the experiments.

2.2. Instrumentation

Cyclic voltammetry(CV) and differential pulse voltammetry (DPV) were performed with a CHI 660D electrochemical work station (Chenhua Co., Shanghai, China) with a conventional three-electrode cell using an Au electrode as working electrode, a platinum wire as counter electrode, and an Ag/AgCl wire as reference electrode (3 M KCl). The working electrodes used in the measurements were successively polished with 0.3, 0.05 μm alumina powder respectively up to the smoothness and then immersed in piranha solution for 10 min (H_2O_2/H_2SO_4, 1:3, v/v), subsequently cleaned with distilled water and absolute ethylalcohol and dried in nitrogen purging prior to each experiment of electrochemical polymerization.

2.3. Preparation of gold nanoparticles functionalized with 3-thiophene acetic acid

All glassware used in the following preparations were thoroughly cleaned in a bath of fresh aqua regia (HNO_3: HCl = 3:1), rinsed in deionized water prior to use. Gold nanoparticles functionalized with 3-thiophene acetic acid (Au NPs-T) were synthesized from a 10 mL aqueous solution containing 0.5 mM $HAuCl_4$ and 5 mM 3-TAA in an ice bath for 30 min, adding 50 μL aqueous solution with 0.8 M sodium borohydride in it subsequently. The solution was stirred for 1 h with grape-red color. The Au NPs-T were respectively washed and centrifuged with water, ethanol three times. Fig. 2 shows the structure of Au NPs-T.

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