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An electrochemiluminescent sensor for dopamine detection based on a dual-molecule recognition strategy and polyaniline quenching

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ABSTRACT

A novel electrochemiluminescence (ECL) sensor was constructed based on a dual-molecular recognition strategy and the quenching effect of polyaniline (PANI) on the ECL emission of graphite-like carbon nitride (g-C_3N_4). The gold nanoparticle-functionalized g-C_3N_4 nanosheets (Au-g-C_3N_4 NS) served as signal probes and as a matrix to immobilize recognition element dithiobis-(succinimidyl propionate) (DSP), capturing dopamine (DA) by the interaction between the amino group of DA and the *N*-hydroxysuccinimide ester of DSP. Next, 3-aminophenylboronic acid functionalized PANI (APBA/PANI) was incubated onto the electrode based on the interaction between the diol of DA and the boronic acid of APBA to achieve an ECL sensor with a sandwich structure. Due to the excellent quenching effect of PANI on the ECL emission of g-C_3N_4, the prepared ECL sensor showed a highly sensitive and linear response to DA in the concentration range of 0.10 pM–5.0 nM, with a detection limit of 0.033 pM. Furthermore, the dual-molecular recognition strategy endowed the sensor with high selectivity. The construction strategy described here provides a new analytical method for the specific detection of small biomolecules.

1. Introduction

Electrochemiluminescence has been widely applied in clinical diagnosis, environmental and food analysis, and immunoassays owning to its low cost, low background emission, and high sensitivity [1]. Several luminophores are used in ECL systems, including Ru composites [2], luminol [3], gold nanoclusters [4], and semiconductor quantum dots such as CdS, CdSe, CdTe, and PbSe [5–8]. However, g-C_3N_4 semiconductors have attracted significant attention because of their particular structure, low-cost synthesis, good water dispersibility, high fluorescent quantum yield, and strong ECL emission [9,10]. Nanoscale g-C_3N_4 materials, such as g-C_3N_4 nanosheets (g-C_3N_4 NS), generally exhibit excellent water solubility and have a high specific surface area. Furthermore, g-C_3N_4 NS are easily integrated with other functional materials such as Cu^{2+} [11], gold nanoparticles (Au NPs) [12], and nonmetal materials [13].

Several ECL quenchers have been studied with the goal of expanding the scope of applications of g-C_3N_4 in ECL. Ferrocene, a metallo-organic compound, efficiently quenches the ECL of g-C_3N_4 by electron and energy transfer [14]. Rutin has been reported as a quencher of g-C_3N_4 ECL, allowing detection of rutin [15]. In addition, metal ions have been used as quenchers of g-C_3N_4 ECL. For example, Cheng et al. achieved sensitive detection of Cu^{2+} based on the quenching effect of Cu^{2+} on the ECL emission of g-C_3N_4 [16]. PANI has been widely used in sensors because of its excellent conductivity, good biocompatibility and stability, non-toxicity, and relatively large surface area [17,18]. However, there are few reports concerning PANI as an ECL quencher. In a previous study, we showed that PANI quenched the ECL of g-C_3N_4 [19], indicating that PANI might be utilized in ECL sensing applications.

DA is a neurotransmitter that plays an important role in human metabolism, the central nervous system, and the endocrine system [20]. A normal level of DA in the body allows typical freedom of movement, whereas extreme abnormalities may cause pituitary tumors, Alzheimer's disease, Tourette's syndrome, Parkinson's disease, and schizophrenia [21]. Therefore, a simple, sensitive, low-cost method for detecting DA is necessary to facilitate accurate and timely clinical diagnosis. Methods currently used for quantitatively measuring DA concentrations, including high performance liquid chromatography-mass spectrometry [22], colorimetric detection [23], electrochemical methods [24], and ECL methods, suffer from low selectivity because of interference by other catechol derivatives and compounds bearing amino groups. Fortunately, this obstacle can be addressed using a dual-molecular recognition strategy,

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in which the target molecule is consecutively recognized by two molecules at different sites [25].

In this study, a sandwich-structured ECL sensor was constructed for detecting DA based on dual-molecular recognition between the amino group of DA and *N*-hydroxysuccinimide ester of DSP, as well as between the diol of DA and boronic acid of APBA/PANI. Au-g-C_3N_4 NS nanocomposites served as a matrix to conveniently load recognition element dithiobis-(succinimidyl propionate) (DSP), which was loaded onto the surface of Au-g-C_3N_4 NS by cleaving the disulfide bond of DSP to form an Au-S bond [26]. DA was captured by exposure to the amine-reactive succinimidyl residues of DSP. Next, APBA/PANI was incubated onto the electrode via chemical recognition between the diol of DA and the boronic acid of APBA. As the amount of DA immobilized on the electrode increased, APBA/PANI was increasingly immobilized, while the ECL intensity decreased. Based on the excellent quenching effect of PANI on the ECL emission of g-C_3N_4, DA detection was achieved with high sensitivity and selectivity. The construction strategy utilized here provides a promising ECL sensing platform for detecting small molecules.

2. Experimental

2.1. Reagents and chemicals

Melamine (2,4,6-triamino-1,3,5-trazine, 99%) was purchased from Aladdin Ltd. (Shanghai, China). Dopamine, aniline and gold chloride tetrahydrate ($HAuCl_4{\cdot}4H_2O$) were obtained from Sigma Chemical Co. (St. Louis, MO, USA). DSP was purchased from Heowns (Tianjin, China). Potassium persulfate ($K_2S_2O_8$) was purchased from Shanghai Chemical Reagent Co. (Shanghai, China). KH_2PO_4 (0.10 M) and $NaHPO_4$ (0.10 M) were used to prepare phosphate-buffered saline (PBS) solution with various pH levels, and 0.10 M KCl was used as a supporting electrolyte. Deionized water was used throughout the experimental process.

2.2. Apparatus

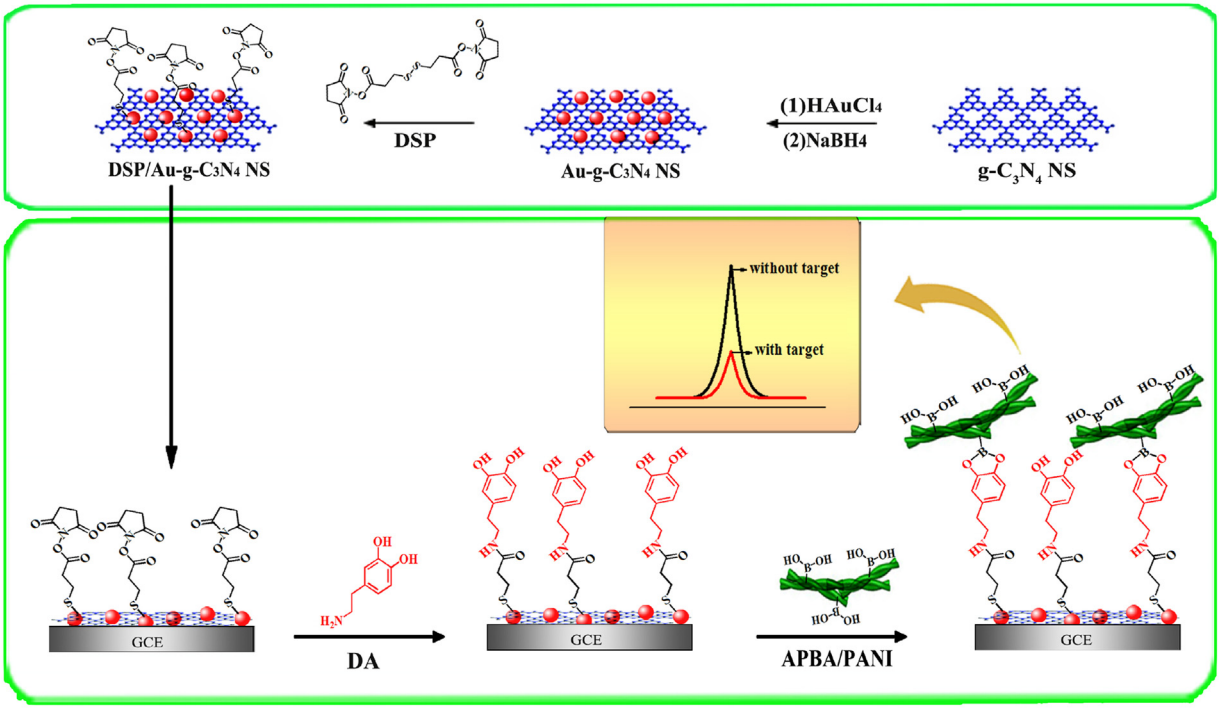
A model MPI-A electrochemiluminescence analyzer (Xi'an Remax Electronic Science & Technology Co., Ltd., Xi'an, China) was used to perform ECL measurements in PBS (0.10 M, pH 7.5). The voltage of the photomultiplier tube (PMT) was set at 600 V. A CHI 600D electrochemical work station (Shanghai Chenhua Instruments Co., China) was employed to perform cyclic voltammetry (CV) measurement in 3.0 mL of 0.10 M PBS (pH 7.5) containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$. Transmission electrode microscopy (TEM, JEM-1200EX) and scanning electron microscopy (SEM, S-4800, Hitachi, Japan) were used to analyze the morphology and size of various nanomaterials. X-ray photoelectron spectroscopy (XPS, Thermoelectricity Instruments, USA) was used to analyze the composition of various nanomaterials. UV–vis (UV–vis) absorption spectra were obtained using a UV-2450 UV–vis spectrophotometer (Shimadzu, Tokyo, Japan). Fourier transform infrared spectroscopy (FT-IR) was performed using a Nexus 670 FT-IR spectrophotometer (Nicolet Instrument).

2.3. Synthesis of g-C_3N_4 NS

As reported previously [27], bulk g-C_3N_4 was synthesized via polymerization of melamine at high temperature. First, 15 g of melamine was added to an alumina crucible and heated at 600 °C for 2 h in a muffle furnace with a heating rate of 5 °C min^{-1}. Bulk g-C_3N_4 was obtained after cooling the heated material at room temperature. Next, 0.20 g of bulk g-C_3N_4 was dispersed in 200 mL deionized water with sonication for 12 h, after which the suspension was filtered to remove residual bulk g-C_3N_4. Finally, the suspension was dried in air to obtain g-C_3N_4 NS.

2.4. Syntheses of Au-g-C_3N_4 NS and DSP/Au-g-C_3N_4 NS

Au-g-C_3N_4 NS were synthesized as follows. First, 1.0 mg of g-C_3N_4 NS were dispersed in 1 mL of deionized water. Next, 10 μL of $HAuCl_4$ solution (1%) was added to the g-C_3N_4 NS dispersion



Scheme 1. Schematic diagrams of the methods used to prepare the ECL sensor and DSP/Au-g-C_3N_4 NS composite.