



Sensitive and selective dopamine sensor based on novel conjugated polymer decorated with gold nanoparticles



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ABSTRACT

A novel surface material was fabricated for the first time at a glassy carbon electrode based on electrochemical polymerization of poly(2,4,6-triaminopyrimidine) (PTAP) decorated with gold nanoparticles (AuNPs). A schematic reaction mechanism was proposed to account for the aggregation of the polymer. The electrochemical performance and surface characterization were achieved employing cyclic voltammetry (CV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and energy dispersive system (EDS). Synergistic effects of the composite hybrid of PTAP and AuNPs promote the catalytic efficiency of the developed (AuNPs-PTAP/GCE) sensor for the electrochemical detection of dopamine (DA). The sensor showed an excellent selectivity for DA quantification with a detection limit of 0.017 μM in electrolytic medium composed of large amounts of ascorbic acid (AA) and uric acid (UA). The sensor was also applied for DA detection in real samples with satisfactory coverage.

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1. Introduction

Conducting polymers with a conjugated π -electron system are booming and dynamic fields for investigation. The electrochemical oxidation of these resonance-stabilized systems has become one of the principal methods for preparing the conjugated and electronically conducting polymers for electronic and steric considerations [1]. Electropolymerization is a good approach to prepare polymer-modified electrodes by adjusting the electrochemical parameters that control film thickness, permeation and charge transport characteristics. One polymer of interest is the pyridine moiety that displays active electron-transporting abilities. They can undergo modification of their optical and electrical properties due to the localized lone pair of sp^2 orbital electrons of the nitrogen atom [2–4]. Moreover, they can be functionalized and tuned depending upon interest and the properties of resultant materials that makes them widely applied in the construction of electrical, optical and biomedical devices. Pyrimidine derivatives are heterocyclic compounds that possess a remarkable biological activity, and have been widely used in fields ranging from the medicinal to industrial applications [5–7]. The amino ($-\text{NH}_2$) group substituted in the pyrimidine rings are acidic components in the hydrogen bonding between the base pairs of nucleic acid responsible for the formation of the double helices in DNA and RNA. Generally, the substituted groups

and monomer backbones have considerable influence over the polymerization processes. In the present work, we have selected 2,4,6-triaminopyrimidine (TAP) as a starting material for the construction of a thin film polymer via reversible potentiodynamic cycles at the glassy carbon electrode. For the best of our knowledge, the fabrication and hence the application of the resulting solid-state poly(2,4,6-triaminopyrimidine) (PTAP) sensor for biological applications are reported for the first time.

Introduction of nanomaterials into conducting polymers have attracted attention in material science since the production of nanoparticles and conducting polymers is simple and easy [8]. The synergistic effect due to the combination of these two valuable materials brings many advantages such as enhanced conductivity [9] and charge transfer kinetics [10]. Additionally, the charge can travel along the conducting polymer chain and transferred to the desired positions via nanoparticles, which bring on an improved electronic activity of the composite material [11].

Particularly, gold nanoparticles (AuNPs) with contributions of their localized surface plasmon resonance improve light absorption, electron transport, excellent conducting properties as well as self-assemble structures [12]. They become convenient candidates for wide range of applications such as solar cells, electronic and biomedical applications [13].

The design of Au-polymer nanocomposites have potential applications in the construction of electrochemical (bio) sensors due to their advantages of enhanced diffusion [14], good stability and biocompatibility

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in biomolecule detection [15], high effective surface area, improved selectivity, sensitivity and outstanding electrocatalytic activity. They function as “electron antennae” efficiently channeling electrons between the electrode and the electroactive species thus promoting the kinetics of electron transfer processes. AuNPs can be immobilized on polymers by dispersive or van der Waals, electrostatic, hydrogen or covalent bonds [16].

There are various efforts toward the development of detection methods for sensitive real-time monitoring of neurotransmitter signaling within biological samples. The signaling of one such neurotransmitter, dopamine (DA) which orchestrates many behaviors such as learning, motivation, and motor control [17]. Its dysfunction has been implicated in multiple diseases such as Parkinson's [18], Schizophrenia [19] and addiction [20]. DA is a peripheral biomarker for the diagnosis of Parkinson's disease [21] and adrenal tumors [22]. The potential of utilizing DA signaling for both diagnostic and basic science applications motivates the development of low-cost tools for monitoring catecholamine at low levels [23,24].

Electrochemical method has a great potential for monitoring of diverse analytes because of its inherent advantages such as fast response, ease of miniaturization, low cost, time saving, high sensitivity, excellent selectivity, and in vivo real-time determination. However, direct detection of DA in the presence of AA and UA at bare electrode is rare due to potential overlap of their voltammetric current peaks and surface fouling caused by adsorption of oxidation products [25,26]. Therefore, modification of electrode surface becomes an important practice to solve this problem and enhance the electrode sensitivity, reproducibility and stability. This work is devoted to construct a sensitive and selective solid-state sensor based on PTAP film decorated with AuNPs for selective determination of DA in the presence of ascorbic acid and uric acid.

2. Experimental

2.1. Chemicals and reagents

All chemicals used are of analytical reagent grade quality and employed as received. The TAP monomer, DA, AA, UA, perchloric acid (HClO_4) and potassium ferro/ferric hexacyanate, all were obtained from Sigma-Aldrich Chemie, Germany. Potassium orthophosphate (KH_2PO_4), dipotassium phosphate (K_2HPO_4) were purchased from BDH, UK. AuNPs (30 nm) (Nanopartz Inc., Loveland, CO, USA) non-covalently capped with citrate ligand used for doping the native PTAP/GCE.

All electrochemical measurements were carried out in 20 mL of 0.1 M phosphate buffer solution (PBS) with $\text{pH} = 7.2$ prepared in Millipore water. The supporting electrolyte degassed with stirring by purging oxygen-free nitrogen gas for 10 min and blanketed throughout the experiment.

2.2. Instrumentation

The electrochemical measurements including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were conducted using a BAS 50W workstation (Bioanalytical System, West Lafayette, IN, USA). The potentiostat was connected to a conventional three electrode cell which consists of the modified glassy carbon electrode (GCE), a platinum coil and an Ag/AgCl (saturated KCl) were all from BAS and used as the working, counter and reference electrodes, respectively. Prior to each experiment, the GCE was polished using a polishing cloth and alumina slurry (5.0 and 1.0 μm), rinsed thoroughly with distilled water, ultrasonicated for 5 min using (JAC Ultra Sonic, 1505, LABKOREA INC, Korea) and finally rinsed with distilled water.

Electrochemical impedance spectroscopy (EIS) was carried out using a Potentiostat (Gamery Instruments, USA) connected to a three-electrode cell. The EIS measurements were conducted at the open

circuit potential in the frequency range from 0.1 Hz to 100 kHz and amplitude of 5 mV.

2.3. Characterization methods for chemical composition and surface morphology

X-ray Photoelectron Spectroscopy (XPS) using an Omicron Nanotechnology XPS system (Germany) was employed to study the chemical state and the relative surface composition of the developed sensor. The obtained XPS spectra were deconvoluted using CasaXPS program (Casa Software Ltd., UK) in which the background was simulated using Shirley function and the peaks were fitted using a Gaussian Lorentzian function.

Atomic Force Microscopy (AFM) (Veeco di Multimode V) is another useful tool to study the surface morphology of the fabricated sensors. The Peak Force Tapping mode using antimony n-doped silicon tip (TAP 525 from Bruker) operated with a resonance frequency of 375–675 kHz and spring constant of <200 N/m. Measurements were conducted on samples with a tip scan rate of 0.5 Hz and 512×512 pixels resolution. Energy Dispersive System (EDS), Aztec and INCA Microanalysis System (Japan), used also for elemental analysis.

2.4. Fabrication of the AuNPs-PTAP/GCE

The clean and polished GCE was dipped in 0.1 M HClO_4 solution containing 10 mM of TAP monomer and the electrode potential was scanned reversibly between 200 and 1800 mV vs Ag/AgCl for 20 cycles at 50 mV s^{-1} . Following the electrodeposition of PTAP film, the electrode was washed carefully, dried and decorated by dropping 20 μL of AuNPs (30 nm) and allowed to be dried at ambient temperature. The resulting sensor (AuNPs-PTAP/GCE) was applied for the simultaneous and selective detection of DA.

2.5. Assay of dopamine in serum and pharmaceutical formulation samples

A serum sample (collected from the University Hospital) was treated with methanol and then centrifuged (Centaur 2, MSE, UK) at 4000 rpm for 15 min. The supernatant was diluted twice with 0.1 M of PBS ($\text{pH} = 7.2$) and then divided into three portions. The first fraction was used for DA determination in the real serum sample, the second and the third portions were containing 0.05 μM of DA in the absence and presence of both AA (100 μM) and UA (10 μM), respectively.

A dopamine hydrochloride injection (Systacare, India) contains 40 mg/mL of original DA solution that was diluted successively with 0.1 M of PBS ($\text{pH} = 7.2$) to a final 0.05 μM of DA in the absence and presence of both AA (100 μM) and UA (10 μM), respectively. The electrochemical measurements and the recovery percent of DA using DPV method were reported to highlight the applicability of the present system for real sample analysis.

3. Results and discussion

3.1. Electrochemical polymerization of PTAP

Fig. 1 depicts the electrochemical polymerization of PTAP film onto GCE by stepping the electrode potential reversibly between 200 and 1800 mV vs Ag/AgCl for 20 cycles at 50 mV s^{-1} in electrolytic solution of 0.1 M HClO_4 containing 10 mM of TAP monomer. A typical anodic peak current obtained at 1400 mV decreases with subsequent cycles indicating the continuous deposition of the polymer. Apparently, an irreversible electrochemical reaction of TPA occurred during the forward and reverse scans where only anodic peak was obtained consistent with the behavior of other pyrimidine derivatives such as methotrexate [27]. It is worthy to note, that the observed peak currents and the electrochemical behavior of pyrimidine materials are sensitive to the electrolytic composition (pH and concentration). In solutions with pH values above 2.0 (data not shown), the peak current response decreased

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