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Electrochemical studies of dopamine under stagnant and convective conditions at a sensor based on gold nanoparticles hosted in poly(triaminopyrimidine)

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ABSTRACT

The catalytic activity of surface materials composed of gold nanoparticles (AuNPs) hosted in poly(triaminopyrimidine) (PTAP) towards dopamine (DA) oxidation was studied under static and hydrodynamic conditions. The hybrid composition of the electrode surface (AuNPs·PTAP) shows a pronounced electron transfer capacity estimated from the application of Nicholson model. The electrochemical behavior of dopamine (DA) is diagnosed by the development of reversible peak currents characteristic for the transfer of two electrons. The apparent diffusion coefficient (D_{DA}^{app}) and the heterogeneous rate constant (k_s) for DA oxidation were estimated using cyclic voltammetry (CV) and chronoamperometry (CA) based on well-known relevant electrochemical theories. The D_{DA}^{app} is found to vary significantly with DA concentrations, [DA], and attain a maximum value of 8.65×10^{-5} cm^2 s^{-1} at 60 μM [DA]. A remarkable value of k_s was obtained at low [DA] and approached a steady value of 4.25×10^{-2} cm s^{-1} above 50 μM [DA]. The estimated thermodynamic and kinetic parameters of DA were compared concurrently with the reported values for possible validation.

1. Introduction

In recent years, considerable attentions have been received towards the development of detection methods that allows sensitive real-time monitoring of neurotransmitters. The neurotransmitter dopamine (DA) in the central nervous system (CNS) controls many behaviors such as learning and motivation [1]. The dopamine dysfunction has been implicated to cause multiple diseases such as Parkinson's [2], schizophrenia [3], and addiction [4]. The neurotransmitter dopamine is concentrated in high amounts (50 nmol/g) in a region of the brain called caudate nucleus [5]. A patient with Parkinson's disease shows approximately complete depletion of DA in caudate nucleus region of brain and hence DA is serving as a marginal biomarker for the diagnosis of Parkinson's disease [6,7]. Moreover, knowing the thermodynamic properties of DA is an important task for pharmaceutical industries to explore drug efficacy and pharmacokinetic studies such as drug release, transport and the extent of absorption [8].

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 [9,10]. However, direct electrochemical detection of DA in presence of ascorbic acid (AA) and uric acid (UA) at bare electrode is rare due to potential overlap of their voltammetric peak currents and also surface fouling caused by adsorption of oxidation products [11,12]. Therefore, modification of electrode surface becomes an important practice to solve this problem and enhance the electrode sensitivity, reproducibility and stability.

Recently, our research group developed for the first time a novel sensor based on the electrochemical polymerization of poly(triaminopyrimidine) (PTAP) at a glassy carbon electrode (GCE) decorated with gold nanoparticles (AuNPs) for the detection of dopamine [13]. The electrochemical performance and surface characterization of the resulting AuNPs·PTAP/GCE sensor were achieved using various techniques. The synergetic properties of PTAP and AuNPs promote the analytical performance of the sensor for simultaneous and selective determination of DA in the presence of AA and UA.

The hydrodynamic technique is an important tool for understanding the electrochemical activities occurred at the solid/liquid interface to evaluate kinetic and thermodynamic parameters. The useful kinetic

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parameters include determination of the apparent diffusion coefficient (D^{app}) and heterogeneous rate constant (k_s) that helps to understand the charge transfer processes at the interface [14–16].

In the present work, composite hybrid surface material (AuNPs·PTAP) was fabricated at a glassy carbon-rotating disk electrode (GCE-RDE) following the same protocol described in our previous studies [13] to evaluate thermodynamic and kinetic parameters for the oxidation of dopamine (DA) under stagnant and convective conditions.

2. Experimental

2.1. Chemicals and reagents

All electrochemical measurements were carried out in 20 mL of 0.1 M phosphate buffer solution (PBS) of pH = 7.2 prepared by mixing appropriate amounts of potassium orthophosphate (0.075 M KH_2PO_4) and phosphoric acid (0.025 M H_3PO_4) from (BDH, UK) prepared in Millipore water. The supporting electrolyte degassed by purging nitrogen gas for 10 min and blanketed throughout the experiment. Chemicals such as triaminopyrimidine (TAP), perchloric acid ($HClO_4$), potassium ferric/ferrous hexacyanate, $[Fe(CN)_6]^{3-/4-}$ and dopamine (DA) (Sigma-Aldrich Chemie, Germany) were analytical-reagent grade and used as received. Gold nanoparticles (AuNPs: 30 nm, Nanopartz Inc., Loveland, CO, USA) non-covalently capped with citrate ligand used for doping the native PTAP previously deposited onto the GCE-RDE.

2.2. Electrochemical experiments

Cyclic voltammetry (CV) and chronoamperometry (CA) experiments were conducted using BAS 50 W workstation (Bioanalytical System, West Lafayette, IN, USA). The electrochemical cell composed of a GCE-RDE with geometric area of 0.071 cm^2, a platinum coil with geometric area of 1.90 cm^2 and an Ag/AgCl electrode (saturated KCl) were all from BAS (Bioanalytical System, West Lafayette, IN, USA) and used as the working, counter and reference electrodes, respectively. The BAS RDE-1 rotating disk electrode assembly was used to connect the working electrode to the potentiostat. Prior to surface modification, the GCE-RDE was polished with alumina powder on a polishing cloth and sonicated successively in water/acetone/water each for 3 min using JAC Ultra Sonic (Korea).

Chronoamperometric (CA) measurements were made by stepping the working electrode potential from −200 mV to +300 mV vs. Ag/AgCl at 50 mV s^{-1} over a range of rotation rates (f = 1000, 2000, 3000, 4000 and 5000 rpm). These rotation rates were selected to maintain a reasonable space and retain the Laminar flow. The anodic potential was held for 20 s at which the current had approached the steady-state value. This approach minimizes the extent to which the number of surface sites will change during the successive additions of [DA]. The last second of digitized data (50 points) was averaged for each experiment and the mean value and standard deviation was recorded.

2.3. Fabrication of the AuNPs·PTAP/GCE-RDE

The clean and polished GCE-RDE was dipped in 0.1 M of perchloric ($HClO_4$) solution containing 10 mM triaminopyrimidine (TAP) and the electrode potential was scanned reversibly between +200 mV and +1800 mV vs. Ag/AgCl for 20 cycles at a scan rate of 50 mV s^{-1} (Fig. 1 of our previous work [13]). Following the electrochemical deposition of poly(triaminopyrimidine) (PTAP) film, the modified 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-RDE) was applied for hydrodynamic analysis to evaluate the kinetic and thermodynamic parameters of dopamine oxidation.

3. Results and discussion

3.1. Construction and catalytic activity of AuNPs·PTAP/GCE

A mechanistic scheme was proposed (shown in the Supplementary file) to account for the buildup and the stepwise assembly of the

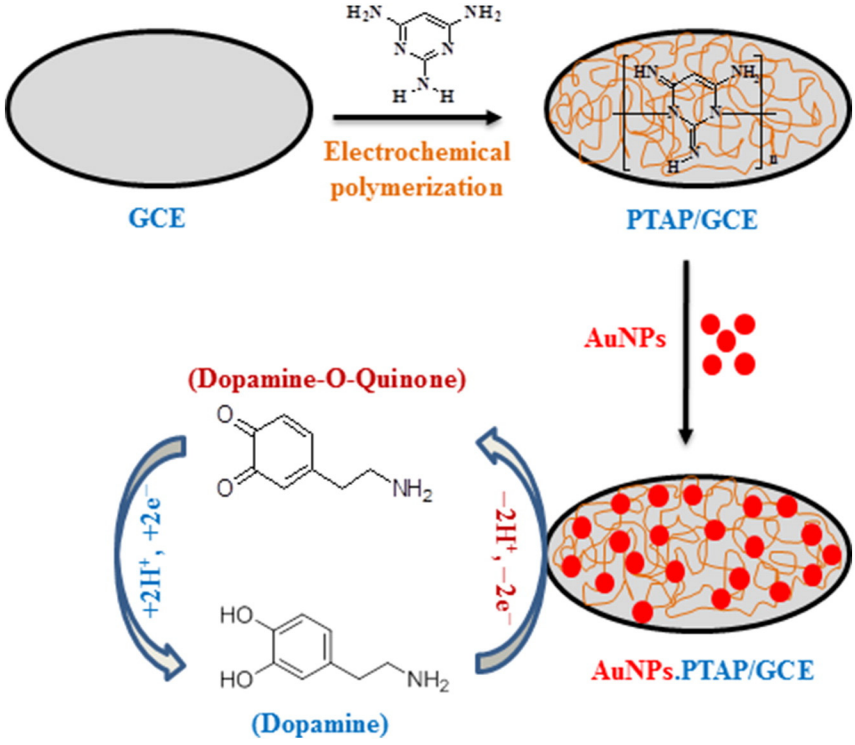

Fig. 1. A schematic diagram demonstrates the construction of AuNPs·PTAP/GCE and its catalytic activity towards DA oxidation.