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Original Article

Delphinidin immobilized on silver nanoparticles for the simultaneous determination of ascorbic acid, noradrenalin, uric acid, and tryptophan

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ABSTRACT

In the present study, the fabrication of a new modified electrode for electrocatalytic oxidation of noradrenalin, based on the delphinidin immobilized on silver nanoparticles modified glassy carbon electrode. Cyclic voltammetry was used to investigate the redox properties of this modified electrode. The surface charge transfer rate constant (k_s) and the charge transfer coefficient (α) for the electron transfer between the glassy carbon electrode and the immobilized delphinidin were calculated. The differential pulse voltammetry exhibited two linear dynamic ranges and a detection limit of 0.40μM for noradrenalin determination. Moreover, the present electrode could separate the oxidation peak potentials of ascorbic acid, noradrenalin, uric acid, and tryptophan in a mixture. The usefulness of this nanosensor was also investigated for the determination of ascorbic acid, noradrenalin, and uric acid in pharmaceutical and biological fluid samples with satisfactory results.

1. Introduction

Noradrenalin (NA) is one of the most important catecholamines secreted in the adrenal medulla and has important physiological roles in the central nervous system [1]. Its role is already proven in increasing the heart rate and blood pressure, dilating the pupils, dilating the air passages in the lungs, and narrowing the blood vessels. Therefore, the quantification of NA in the biological system provides essential information about its adverse physiological effects such as anxiety, diabetes, pain, heart disease, and other neurological disorders such as Parkinson and Alzheimer diseases [2].

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Ascorbic acid (AA; also called vitamin C) is widely used in the food industry as an antioxidant to prevent undesirable changes in color, taste, and odor [3]. This compound exists widely in food, plants, and animal tissues, and has an important role in preventing infectious diseases; however, it cannot be synthesized by the human body [4].

Uric acid (UA) is a very important biomolecule; it is a major nitrogenous compound in urine, a primary product of purine metabolism in the human body, and is of biomedical significance [5]. This compound has important roles in human metabolism, the central nervous and renal systems, and its high quantities in serum and urine can provide information about some important diseases such as gout, leukemia, kidney damage, and infectious disease [6].

Tryptophan (Trp) is an essential amino acid with numerous physiological roles; it functions independently or by incorporation into the structure of larger molecules or polymers such as proteins [7]. In addition, this compound has a significant role in the mechanism of brain functions [8]. Tryptophan is commonly added to dietary food products as a food fortifier and in pharmaceutical products because of its scarce presence in vegetables and lack of ability of the body to produce it [9]. Toxic products can accumulate in the brain as a result of the improper metabolism of Trp, which can then cause problems such as hallucinations, delusions, and schizophrenia [10].

Ascorbic acid has several functions in the brain and neurons and has been verified to enhance the synthesis of neuronal catecholamine [11] and noradrenalin [12]. By contrast, UA and AA coexist in biological fluids such as blood and urine. Human studies have reported a reverse association between plasma AA or vitamin C intake and serum UA quantities [13]. In the presence of AA, Trp can also be converted into 5-hydroxytryptophan, which forms serotonin, an important brain chemical in animals. Therefore, the determination of Trp and AA concentration in animal blood could aid in the control of the production of serotonin in the body [14].

The aforementioned topics demonstrate that the simultaneous determination of AA, NA, UA, and Trp is of critical importance in the field of biochemistry and neurochemistry, and in diagnostic and medical investigations. However, with conventional bare electrodes, the simultaneous determination of these compounds is very difficult because of the overlap of their oxidation potentials; therefore, modification of the electrode is necessary and many modifiers have been used for the same purpose [15–18]. Metal nanoparticles such as silver nanoparticles have been widely used in modified electrodes. They are small and have good conductivity and excellent catalytic activity, which make them a decent candidate in the preparation of electrochemical nanosensors and nanobiosensors [19–21]. Moreover, quinones are fundamentally important in the modification of electrodes [22–24]. Their fundamental role in biological electron transport and in industrial processes as redox catalysts is proven. Delphinidin has an o-quinone ring (Figure 1), which makes it a good material for modifying electrodes. It is an anthocyanidin, a primary plant pigment, and an antioxidant [25].

In this work, we report for the first time that the delphinidin silver nanoparticles modified glassy carbon electrode (DSNPs-GCE) exhibited a strong catalytic activity for the oxidation of NA, and resolved the voltammetric responses of AA, NA, UA, and Trp compounds into individual signals. The DSNPs-GCE has several advantages such as wide linear concentration ranges, excellent stability, technical simplicity, good reproducibility, and good detection limit for NA. This nanosensor was successfully used for the simultaneous determinations of AA and NA in commercial pharmaceutical samples and UA in a urine sample.

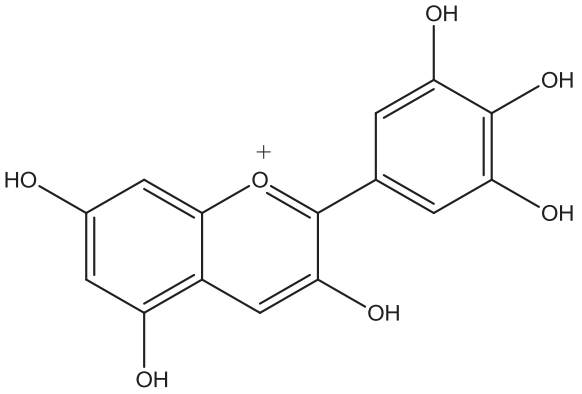

Figure 1 – The molecular structure of delphinidin.

2. Methods

2.1. *Materials and instruments*

Noradrenalin and delphinidin chloride were purchased from Sigma–Aldrich (St Louis, MO, USA). Silver nitrate, nitric acid, AA, UA, tryptophan (Trp) and other reagents, obtained from Merck (Darmstadt, Germany), were of analytical grade and were used as received. Noradrenalin injection solution (1 mg/mL; from Bio and Pharma Companies, Brussels, Belgium) and vitamin C tablet (500 mg, from Pharma Chemie, Tehran, Iran) were purchased from approved local companies at the drugstore. A phosphate buffer solution (0.10M) was prepared with

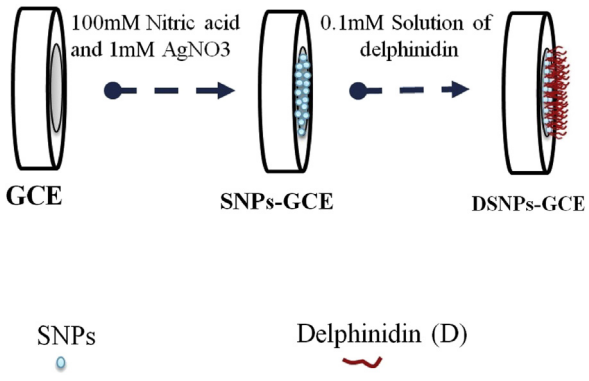

Figure 2 – Fabrication steps of DSNPs-GCE. $AgNO_3$ = silver nitrate; GCE = glassy carbon electrode; DSNPs-GCE = delphinidin silver nanoparticles modified glassy carbon electrode; SNP = silver nanoparticle.