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Electroanalysis of ascorbic acid (vitamin C) using nano-ZnO/poly(luminol) hybrid film modified electrode

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ABSTRACT

Electrochemical analysis of ascorbic acid (AsA) in physiological condition using a new hybrid film modified electrode is described. Electrochemical polymerization of luminol in 0.1 M H_2SO_4 solution was carried out using ZnO nanoparticles (ZnO-NPs) coated glassy carbon electrode (GCE) as working electrode. This hybrid film coated electrode noted as poly(luminol)/ZnO-NPs hybrid film modified GCE (PLu/ZnO-NPs/GCE). The atomic force microscope (AFM) and scanning electron microscope (SEM) studies were demonstrated that PLu/ZnO-NPs hybrid film covered the electrode surface and the ZnO-NPs particle sizes were <100 nm. The visible blue colored organic–inorganic (PLu/ZnO-NPs) hybrid films were observed on the electrode surface. Electrochemical studies proved that PLu/ZnO-NPs hybrid film modified electrode is electroactive in the pH range from 1 to 11 and the poly(luminol) (PLu) redox peak was pH dependent with a slope of −53 mV/pH. The PLu/ZnO-NPs modified electrodes electroactivity also investigated by catalyzing the oxidation of AsA, demonstrating its great potential applications in electroanalysis of AsA. The resulting, AsA electrochemical sensor exhibited a wide linear response range (from 1×10^{-6} to 3.6×10^{-4} M, $r^2 = 0.9989$), lower detection limit (1×10^{-6} M) and fast response time (3 s) for AsA determination. Our results show that PLu/ZnO-NPs hybrid film provides a novel and efficient platform for the oxidation of AsA and realizing efficient electrocatalysis and that the materials have potential applications in the fabrication of electrochemical sensors. Analysis of commercial vitamin C samples using PLu/ZnO-NPs hybrid film modified electrode was demonstrated and the obtained results are good agreement with the labeled amount.

1. Introduction

The term 'vitamin C' refers to both ascorbic acid (AsA) and dehydroascorbic acid, since the latter oxidation product is reduced back to ascorbic acid in the body. AsA is well known for its radical-scavenging capacity and is the most effective water-soluble antioxidant in human plasma. It is the terminal small molecule antioxidant in many biological systems and probably the most abundant free radical scavenger in many cell types. In addition to its role as an antioxidant, the moderately positive standard redox potential of the ascorbate/monodehydroascorbate couple makes ascorbate an excellent one-electron donor to a large variety of enzymes, in particular, oxygenases and hydroxylases [1]. Fresh fruits (especially citrus fruits and black currant) and green vegetables constitute rich sources of AsA. Human milk provides enough AsA to prevent scurvy in breast-fed infants. AsA (L-*threo*-hex-2-enono-1,4-lactone) is a diacid ($pK_1 = 4.2$ and $pK_2 = 11.8$), which exists almost exclusively as the monoanion at physiological pH values [1,2].

Due to the importance of AsA in life cycle, its determination in aqueous solution is very important. Traditional procedures for AsA determination are generally based on enzymatic methods [3], on titration with oxidizing agents, like iodine or 2,6-dichlorophenolindophenol [4] and HPLC analysis with fluorimetric [4] or UV–vis detection [5,6]. Recently there is a considerable interest to develop chemical sensors for electrochemical detection of AsA. AsA can be easily oxidized electrochemically at conventional electrodes which have been used to detect AsA [7–15]. However, direct oxidation of AsA at bare electrode results in adsorption of the oxidized product on the electrode surface; it causes electrode fouling and unstable electrode response [11–15]. In addition, some of biological molecules, e.g. dopamine and uric acid undergo oxidation within same potential window as AsA. To ignore these problems, modified electrodes have been developed and reported for detection of AsA with various functional groups at lower oxidation potential [16–23].

Nanocomposites made of inorganic materials and redox polymers are possessing good mechanical strength, thermal and chemical stability. In addition to those applications, many recent efforts have centered on the design of other types of hybrid materials

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which explore in various fields, for example: electrocatalysis, transducers, biomaterials, etc [24]. The embedding of inorganic nanoparticles into polymers represents a simple way to protect nanoparticles from agglomeration and take advantage of their physical characteristics [25]. Hybrid nanocomposite systems based on the nanoscaled dispersion of an inorganic phase in a thermally stable polymer matrix have attracted extensive research interest in recent years [26–30].

Zinc oxide (ZnO) has a broad range of applications, e.g. in pigments, rubber additives, gas sensors, varistors and transducers. ZnO-NPs are increasingly being used as pigments and UV absorbers in personal care products, coatings and paints, predominantly because of their UV absorbance efficiency and transparency to visible light. As a wide bandgap semiconductor material with a large excitation binding energy, ZnO has been promising applications in catalytic, electrical, optoelectronic, photochemical fields and sensors [31–35]. ZnO-NPs offers several advantages over existing biosensing platforms, most notably a large surface area for greater biofunctionalization [36] and the interest has been focused towards the applications of ZnO-NPs in chemical and biosensing because of its high isoelectric point (9.5), biocompatibility and fast electron transfer kinetics [37].

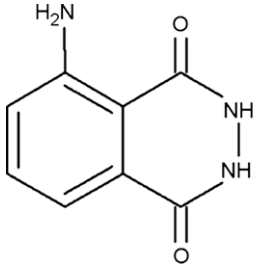
The 5-Amino-2,3-dihydro-phthalazine-1,4-dione (Luminol) (Scheme 1) has widely used in chemistry and biochemistry [38]. Furthermore, luminol has been extensively used in chemiluminescence detection [39–41] and electrochemiluminescence [42–45]. An amino group in luminol serves as electron-donating group due to its positive mesomeric effect and enhances the chemiluminescence intensity resulting from reactions on the hydrazide group.

In the present paper, a new hybrid material (PLu/ZnO-NPs) coated electrodes preparation; characterization and its potential application in electrocatalysis of AsA were reported. PLu/ZnO-NPs hybrid film was characterized using atomic force microscope (AFM) and scanning electron microscope (SEM). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) have been used to investigate the electrochemical properties. To the best of our knowledge, for the first time, PLu/ZnO-NPs hybrid film coated electrode has been used for electroanalysis of AsA in physiological condition. In addition, analysis of commercial vitamin C tablets was investigated using the proposed method.

2. Experimental

2.1. Apparatus

Electrochemical measurements were performed with CH Instruments (TX, USA) Model-400 potentiostat with a conventional three-electrode cell. A BAS GCE or ZnO-NPs/GCE was employed as working electrodes. Platinum wire is used as auxiliary electrode. All the cell potentials were measured with respect to an Ag/AgCl [KCl (sat)] reference electrode. Amperometric studies were performed on a Bi-potentiostat Model CHI750A (TX, USA) having an analytical rotator model AFMSRK with MSRX speed control (PINE Instruments, USA). Hitachi scientific instruments (London, UK) Model S-3000H scanning electron microscope was used for surface image measurements. The AFM images were recorded with a multimode scanning probe microscope system operated in tapping mode using model CSPM4000 Instruments, Ben Yuan Ltd. (Beijing, China). Electrochemical impedance measurements were performed using an impedance measurement unit, IM6ex ZAHNER, Messsysteme (Kroanch, Germany). All the pH measurements were performed on Suntex Model SP-701 pH meter (Jiangsu, China). All the experiments were carried out at an ambient room temperature of 25 ± 2 °C.



Scheme 1. Chemical structural formula of luminol.

2.2. Reagents

All chemicals were of analytical reagent grade unless otherwise specified. Luminol was purchased from Aldrich (Milwaukee WI, USA) and used as received. Dopamine hydrochloride, uric acid and ZnO-NPs (<100 nm) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Sulfuric acid and sodium hydroxide were purchased from Wako pure chemicals (Osaka, Japan). Ascorbic acid, sodium acetate and sodium dihydrogen phosphate were received from E-Merck (Darmstadt, Germany) and used without further purification. Water was obtained from a Millipore Alpha-Q Lotun ultrapure water system (18 MΩ resistivity). Solutions and buffers were prepared employing standard laboratory procedures. Before each experiment the solutions were deoxygenated by purging with pre-purified nitrogen gas. Vitamin C tablets were purchased from a local drug store in Taipei.

2.3. Modified electrode preparation

ZnO-NPs suspension was prepared by dissolving 10 mg of accurately weighed ZnO-NPs in 10 ml dimethyl formamide and then ultrasonicated for 10 min to create a homogenous suspension. Prior to the electrode modification, the GCE was mechanically polished with alumina powder (Al_2O_3, 0.05 μ) up to a mirror finish and ultrasonicated in distilled water for 5 min. Then GCE was electrochemically activated by using 10-times cyclic potential sweeps in the range from −0.5 to 1.0 V in 0.1 M H_2SO_4 solution at a scan rate of 0.1 Vs^{-1}. The mixture of 10 μl ZnO-NPs suspension was spread evenly onto the surface of pretreated GCE which was dried for 3 h in the absence of light; the solvents evaporated and left the ZnO-NPs on the electrode surface. Finally, the ZnO-NPs modified electrode was thoroughly rinsed with double-distilled water. Thereafter, ZnO-NPs/GCE electrode was cycled in 0.1 M H_2SO_4 solution containing 0.5 mM luminol between the potential ranges from 0.0 to 1.0 V for 20 cycles. Afterwards, the electrode was thoroughly rinsed with double-distilled water and then dried at room temperature for an hour in the absences of light. When not in use, the electrode was stored in aqueous solution of 0.1 M phosphate buffer solution (PBS, pH 7.0) at 4 °C. It was noted as PLu/ZnO-NPs/GCE and then used for further studies. For comparison, ZnO-NPs/GCE and PLu/GCE were prepared and used for further investigation.

3. Results and discussion

3.1. Electrochemical polymerization of luminol

Fig. 1 shows consecutive cyclic voltammograms (CVs) of luminol polymerization on ZnO-NPs modified GCE from 0.1 M H_2SO_4 solution containing 0.5 mM luminol. On the first anodic scan an oxidation peak was observed at +0.93 (Pa_1) which is corresponding