A highly sensitive sensor for simultaneous determination of ascorbic acid, dopamine and uric acid based on ultra-small Ni nanoparticles

Wenya He, Yu Ding, Wenqing Zhang, Lifei Ji, Xin Zhang *, Fengchun Yang *

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710127, China

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ABSTRACT

A highly sensitive sensor based on carbon-supported Ni nanoparticles (Ni/C) with ultra-small size was prepared for the simultaneous determination of ascorbic acid (AA), dopamine (DA) and uric acid (UA). The electrochemical response showed excellent electrocatalytic activity toward the oxidation of AA, DA and UA with three well defined oxidation peaks and larger peak separation. Meanwhile, using the ultra-small Ni nanoparticles modified electrode with differential pulse voltammetry (DPV) method, the linear response ranges for the determination of AA, DA and UA were 20–2400, 1–55 and 5–180 μM in the coexistence systems of these three species under optimum condition and the detection limits (S/N = 3) were 5, 0.05 and 0.1 μM, respectively. Especially a much higher sensitivity for Ni/C modified electrode compared to other electrodes was also observed. Moreover, satisfactory results were achieved for the determination of AA, DA and UA in vitamin C tablet, DA hydrochloride injection, fetal bovine serum and human urine samples. The results demonstrated that the electrochemical sensor developed from the ultra-small Ni nanoparticles had advantages of high sensitivity and good selectivity for practical applications.

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1. Introduction

As known, ascorbic acid (AA), dopamine (DA) and uric acid (UA) have significant functions in organism [1,2], and are considered as crucial molecules for physiological processes in human metabolism [3,4]. They usually coexist in biological matrixes. Therefore, simultaneous determination of AA, DA and UA has received a great deal of attention. Several methods have been developed for the purpose such as chemiluminescence [5], high-performance liquid chromatography [6], electrochemical method [7,8], ultraviolet–visible spectroscopy [9] and capillary electrophoresis [10]. Among these methods, electrochemical method has been drawn tremendous attention due to the advantages of simplicity, rapidity and high sensitivity [11]. However, the overlap of their voltammetric responses, the pronounced electrode fouling, poor selectivity and reproducibility make their simultaneous determination highly difficult [12].

To overcome these problems, the electrodes were modified by various materials, such as polymers [13–15], nanoparticles [16–18], metal complexes [19,20] and organic redox mediators [21,22]. Metallic nanoparticles, especially noble metal nanoparticles modified electrodes, have attracted much more attention in electroanalysis because of their high electrocatalytic activities [23,24]. But many of the noble metals exhibit unsatisfactory sensitivity, poor selectivity and easy poisoning by

adsorbed intermediates, which are a critical issue for practical applications [23]. The aim of recent work, therefore, is to enhance the sensitivity of the sensor by investigating more active and lower cost replacements to noble metal nanoparticles.

Recently, more and more interests have been focused on transition metal nanoparticles because of their multiple oxidation states for electron-transfer processes. Especially, nickel nanoparticles (Ni NPs) have been extensively used in electrode modification because of their inherent electrocatalytic activity for oxidation reactions, which is based on mediation redox reaction of $Ni(OH)_2/NiOOH$ on the electrode surface [25], as well as their good stability, mechanical strength, rapid electron transport and low cost [26,27]. Liu et al. [28] developed a nonenzymatic glucose sensor based on the renewable Ni NPs-loaded carbon nanofiber paste (NiCFP) electrode. Yu et al. [27] improved the sensitivity of sensors for Phenobarbital determination using uniform Ni NPs. Chen et al. [29] developed a novel imprinted electrochemical sensor based on Ni NPs-graphene modified electrode for the determination of tetrabromobisphenol A. Zhang et al. [30] prepared Ni NPs-carbon nanotubes hybrid to fabricate paste electrodes for electrochemical sensing of carbohydrates. About the Ni facilitates the catalytic reaction, it is closely related to the cases of filling d orbit. According to the Band model, the metal atoms that bonded to each other can be derived from the interaction of positive charged ions and valence electrons. The electrons of atomic in the core layer are localized, and valence electrons in atoms of different energy levels compose the energy bands. For transition metal, there is overlap between the s belt and d belt, thus affect the

* Corresponding authors.
E-mail addresses: zhangxin@nwu.edu.cn (X. Zhang), fyang@nwu.edu.cn (F. Yang).

degree of filling d electrons. Usually, it should be filled 3d band with 10 electrons, but for nickel, due to the 3d and 4 s band overlap, only partially get into the 3d band, the other portion into 4 s band resulting a "d band holes". For the catalytic reaction, the presence of d band holes makes metal have the ability to accept electrons from the outside and adsorbed species with band construction. In general, the catalytic activity of transition metal in the periodic table from left to right in the order of decreasing, mainly because the degree of filling of the transition metal d orbit increased successively. Nickel, located in VIII, due to electronic number did not filled in the d orbit, which made the higher catalytic activity for the possibility of facilitating the sensing (Scheme 1).

Considering excellent performances as described above, in this work, Ni NPs (diameter: ~5 nm) were synthesized by controlled reduction in oleylamine and dispersed on carbon black to develop carbon-supported Ni NPs (Ni/C) for simultaneous determination of AA, DA and UA. Oleylamine, used here as solvent and surfactants for NPs stabilization, can reduce the diffusion rate of the as-prepared particles to prevent aggregation, and restrict the NPs growth to get an ultra-small size. It is particularly worth mentioning here that we get the NPs with very small size compared with above reported work, which will make nanoparticles get larger specific surface area for the extraordinary electrocatalytic activities and higher sensitivity. The crystal structures of the Ni NPs were characterized by X-ray diffraction (XRD) and the morphology characteristics of Ni/C was studied in details with transmission electron microscope (TEM). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were employed to investigate the electrochemical behaviors of AA, DA and UA at the proposed Ni/C modified electrode (Ni/C/GCE). Based on the different electrocatalytic activities of the Ni/C/GCE toward AA, DA and UA, a sensitive and selective method for these three molecules was well established and further used in real sample analysis. To the best of our knowledge, electrochemical sensors for simultaneous determination of AA, DA and UA based on Ni NPs with such small size have not been reported yet.

2. Experimental

2.1. Reagents and materials

Ni(acac)$_2$, oleylamine (OAm, technical grade, 70%, Aldrich), oleic acid (OA, technical grade, 90%, Aldrich), carbon black (Kejen EC 300J). Nafion (5 wt.%) was purchased from Sigma-Aldrich. AA, DA, UA and N,N-dimethylformamide (DMF) were from Alfa Aesar. 0.1 M phosphate buffer solution (PBS) was employed as supporting electrolyte. Rod GCEs were from the Chenhua Co. Ltd. (Shanghai, China). All other chemicals and reagents for electrochemical measurements were of analytical grade without further purification. Real samples including vitamin C tablet, DA hydrochloride injection, fetal bovine serum and human urine. The deionized water for solution preparation was from a Millipore Autopure system (18.2 MΩ, Millipore Ltd., USA).

2.2. Preparation of Ni/C nanoparticles

Under a nitrogen flow, 129 mg of Ni(acac)$_2$ (0.5 mmol) was mixed with 10 mL oleylamine (OAm) and 0.32 mL (1 mmol) oleic acid (OAc). The formed solution was heated to 110 °C in 20 min, resulting in a nice green solution (Ni-oleate complex formation). The solution was degassed at 110 °C for an hour. Next, after 200 mg of borane tributylamine complex (BTB) solvated in 2 mL of OAm quickly injected into the solution, the solution was cooled down to 90 °C. Then, a visible color change from green to a dark-brown was observed. The resultant solution was kept at 90 °C for 60 min. The solution was cooled down to room temperature. 30 mL of ethanol was added and the product was separated by centrifugation (8000 rpm for 8 min). The product was then dispersed in hexane.

2.3. Preparation of Ni/C/GCE

The Ni/C as prepared was modified on GCE by general drop-coating method. As following, before the modification, a GCE was polished with 0.05 μM α-Al$_2$O$_3$ powder, and then ultrasonically rinsed by ethanol and deionized water, then dried at room temperature. 5 mg Ni/C was dispersed in 6 mL DMF and 50 μL Nafion (0.1%, v/v, diluted from the 5% Nafion solution) using high frequency ultrasonic to form Ni/C suspensions. 60 μL Ni/C suspensions was dropped onto the GCE and dried under infrared lamp subsequently to finish the modification.

2.4. Apparatus

All the electrochemical measurements were carried out using a CHI 660D electrochemical workstation (CH Instruments, Shanghai, China). A conventional three-electrode system, consisting of a modified GCE as the working electrode (electrode area: 0.071 cm^2), a saturated Ag/AgCl electrode as reference electrode, and a platinum wire as auxiliary electrode, were employed. Morphologies of Ni NPs were determined using TEM (Tecnai G2 F20 S-TWIN, FEI, America). Electrochemical impedance spectroscopy (EIS) was performed with the same three-electrode configuration in an electrolyte solution of 0.1 M KCl containing 1.0 mM $[Fe(CN)_6]^{4-/3-}$, in a frequency range from 0.1 to 10^5 Hz with an AC probe amplitude of 50 mV. X-Ray Diffraction (XRD) profiles were obtained (D8 AdVance, Bruker) with high-intensity Cu Kα radiation ($\lambda = 1.5406$ Å).

2.5. Preparation of samples

2 tablets of vitamin C (labeled 100 mg vitamin C per tablet) were completely ground and homogenized. Then, the powder was dissolved by sonication for 5 min in 50 mL of water. Finally, 100 μL of the solution plus 20 mL of the buffer (pH 7.0) was used for analysis. 12.5 μL of dopamine hydrochloride injection solution (10 mg mL^{-1}) was diluted to 25 mL with water. Then, 20 μL of this diluted solution was injected into 20 mL PBS (pH 7.0), and determined according to the recommended
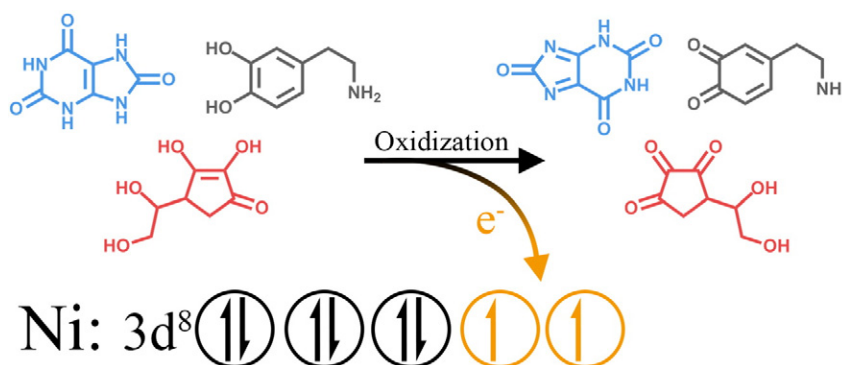
Scheme 1. The mechanism of Ni nanoparticles in facilitating the sensing.