Analytica Chimica Acta 819 (2014) 94–101

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Nonenzymatic amperometric sensor for ascorbic acid based on hollow gold/ruthenium nanoshells

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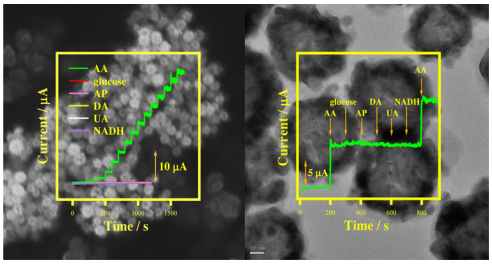
HIGHLIGHTS

- We synthesized hollow gold/ruthenium (hAu–Ru) nanoshells for ascorbic acid sensing.
- The hAu–Ru nanoshells showed sensitivity of 426 μA mM^{-1} cm^{-2} for ascorbic acid.
- Good selectivity against glucose, uric acid, dopamine, 4-acetamidophenol, and NADH.
- The linear dynamic range appeared from zero to 2.0 mM (R = 0.9995).
- Response time (1.6 s) and low detection limit (2.2 μM) were obtained at pH 7.40.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 21 January 2014
Accepted 12 February 2014
Available online 15 February 2014

Keywords:
Hollow gold ruthenium
Nonenzymatic ascorbic acid sensor
Electrocatalyst
Amperometric sensor
Biosensor

ABSTRACT

We report a new nonenzymatic amperometric detection of ascorbic acid (AA) using a glassy carbon (GC) disk electrode modified with hollow gold/ruthenium (hAu–Ru) nanoshells, which exhibited decent sensing characteristics. The hAu–Ru nanoshells were prepared by the incorporation of Ru on hollow gold (hAu) nanoshells from Co nanoparticle templates, which enabled AA selectivity against glucose without aid of enzyme or membrane. The structure and electrocatalytic activities of the hAu–Ru catalysts were characterized by spectroscopic and electrochemical techniques. The hAu–Ru loaded on GC electrode (hAu–Ru/GC) showed sensitivity of 426 μA mM^{-1} cm^{-2} (normalized to the GC disk area) for the linear dynamic range of <5 μM to 2 mM AA at physiological pH. The response time and detection limit were 1.6 s and 2.2 μM, respectively. Furthermore, the hAu–Ru/GC electrode displayed remarkable selectivity for ascorbic acid over all potential biological interferents, including glucose, uric acid (UA), dopamine (DA), 4-acetamidophenol (AP), and nicotinamide adenine dinucleotide (NADH), which could be especially good for biological sensing.

1. Introduction

Ascorbic acid (AA, generally known as Vitamin C) and its salts are commonly used for food additives. AA, widely known as antioxidant, also plays a key role in metabolism of cholesterol. In recent

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http://dx.doi.org/10.1016/j.aca.2014.02.017
0003-2670/

researches, a variety of important role of AA has been revealed in various fields such as toxicology, genetics, oncology, nutritional science, and even material science [1] as a mild reducing agent. Toxicity of reactive oxygen species [2] and synthetic pyrethroid pesticide [3] can be protected by AA reducing toxic substances. Thus, measuring AA is of great importance from food industry to medical reason. In fact, a tremendous number of studies have been reported for quantification of AA. For example, colorimetry, titrimetry, fluorometry, high performance liquid chromatography, chemiluminescence, flow injection method, and electrochemical measurement were reported [4].

While AA is important in biological process, it is also known as one of the notorious biological interfering species in detection of other biomolecules, e.g., glucose and neurotransmitters [5]. Despite of various determination methods of AA, the electrochemical methods, including amperometric [6,7], voltammetric [8,9], and potentiometric [10] methods, are considered as one of the convenient methods due to simplicity and rapidity without sample preparation procedures. Most of reported electrochemical works use either enzyme (ascorbate oxidase), mediator or conducting polymer [5] to overcome the irreversible nature of AA oxidation and enhance the selectivity and sensitivity for determination of AA.

Recently, nanostructured catalysts have been applied to nonenzymatic electrochemical biomolecule sensors since the pioneer works of glucose detection with nanoporous platinum [11–13]. For the nonenzymatic electrochemical detection of AA, uric acid (UA), and/or dopamine (DA), palladium materials were often applied via incorporation with carbon nanotube, carbon nanofiber, polymer and graphene [5,8,14–17]. 3-D nanoporous gold film was also used for electrochemical determination of DA and AA [18].

Gold nanoparticles (Au NPs) have been well known as nonenzymetic glucose oxidation catalysts [19]. However, there were some reports for AA sensing based on Au NPs [20–22], where interference by glucose were not explicitly shown up to the physiological level. Glucose is also interfering species in AA sensing, and vice versa. Meanwhile, the oxidation current of glucose decreased by plating Ru layer [23] and potential of glucose was shifted depending on the amount of incorporating Ru [30] in Au-based glucose sensing. Thus, Ru modification on the surface of Au nanoshells is one of the plausible ways to overcome glucose interference in AA sensing.

In this study, we report a new nonenzymatic amperometric AA sensor modified with the hollow gold/ruthenium (hAu–Ru) bimetallic nanoshells, which shows high selectivity for AA over possible biological interferents, including UA, DA, 4-acetamidophenol (AP), and nicotinamide adenine dinucleotide (NADH) as well as glucose, at the physiological pH. This is rare case for the gold based catalyst without aid of enzyme or membrane.

2. Experimental

2.1. Reagents

The materials and reagents used in this work are as follows: $CoCl_2{\cdot}6H_2O$, trisodium citrate ($Na_3C_6H_5O_7$), $RuCl_3{\cdot}xH_2O$, D-(+)-glucose, L-ascorbic acid (AA), 4-acetamidophenol (AP), dopamine hydrochloride (DA), uric acid (UA) and β-nicotinamide adenine dinucleotide reduced disodium salt hydrate (NADH) were purchased from Sigma–Aldrich (St. Louis, MO); $NaBH_4$ and $HAuCl_4{\cdot}xH_2O$ were purchased from Fluka (Buchs, Switzerland) and Alfa Aesar (Haverhill, MA), respectively. All other conventional chemicals used were of analytical grade. All aqueous solutions were prepared using deionized water (resistivity $\geq$18 MΩ cm^{-1}).

2.2. Synthesis of hAu–Ru nanaoshells

Before synthesizing hAu–Ru nanoshells, the hAu nanoshells were synthesized at room temperature using a slightly modified method reported in the literature [24,25]. In a typical synthesis of hAu nanoshells, 135 mL of deionized water was placed in a 250 mL beaker and situated to a nitrogen atmosphere by inserting a syringe needle over 30 min with vigorous stirring. Then, 2.5 mL of $NaBH_4$ (0.24 M) and 2.5 mL of trisodium citrate (0.12 M) were injected into water sequentially. After waiting for 5 min, 5.0 mL of $CoCl_2$ (75 mM aqueous solution) was added drop by drop while stirring and then left to stand with stirring for a while (ca. 15 min). The reaction mixture became dark brown in color at this stage due to formation of Co nanoparticles. Then 5 mL of $HAuCl_4$ aqueous solution (30 mM) was added drop-wise to obtain hAu nanoshells, where the color changed to dark blue. The hAu nanoshells were collected after 15 min by washing-centrifugation at least five times. To prepare hAu–Ru nanoshells, 5 mL of $RuCl_3$ aqueous solution (30 mM) was added drop by drop to the aforementioned product solution after 5 min (containing hAu nanoshells) and left to stand for 15 min while stirring, where the color of the solution was changed back to dark brown due to excess $RuCl_3$. The obtained samples were washed at least five times with water and collected by centrifugation for morphology and structure analysis.

2.3. Characterizations

For high-resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray spectroscopy (EDS) and field emission scanning electron microscope (FE-SEM) sample preparation, one drop of an aqueous suspension of the nanostructures was placed on a carbon-coated copper grid (Ted Pella, Redding, CA), and allowed to dry. TEM was performed using a JEOL JEM-2100F (Cs-corrected STEM/TEM) microscope at an accelerating voltage of 200 kV. The hAu and hAu–Ru nanoshells were also characterized by scanning electron microscopy (SEM). Raman scattering measurements were directly carried out with hAu–Ru nanoshells on a transferred to a Pyrex glass slide. The backscattering configuration was employed to record the Raman spectrum using a confocal microscope with a 100× (0.9 NA) objective in focused the laser beam (~1 μm) with 632.8 nm He–Ne laser light. We kept with lower laser power to prevent from the decomposition of the sample by localized laser heating. Optimal results were obtained with 20 mW laser power and 300 s integration times. The surface properties were characterized using X-ray photoelectron spectroscopy (XPS, Theta Probe AR-XPS System, Thermo Fisher Scientific) at Busan Center, KBSI. Crystal structures were studied by X-ray diffraction (XRD; Siemens D500, with a Cu Kα radiation).

2.4. Electrochemical measurements

To increase the signal-to-noise ratio (S/N) all the electrochemical experiments were carried out in a Faraday cage under the nitrogen atmosphere using a CHI 705 workstation (CH Instruments, TX, USA) and an RDE-1 (BAS (Bioanalytical Systems Inc., IN, USA)). For measurements, a Pt coil and saturated calomel electrode (SCE) were used as a counter and reference electrode, respectively, with a conventional three-electrode cell. A glassy carbon (GC) electrode (3 mm in diameter, BAS) was used as the substrate electrode to modify the surface with hAu or hAu–Ru nanoshells, which served as a working electrode. Prior to modification of the electrode surface, a GC electrode was wet-polished on a microcloth pad (Buehler) using 0.3 μm alumina slurries. The electrode was cleaned with deionized