



Electrochemical synthesis of Ag nanoparticles supported on glassy carbon electrode by means of *p*-isopropyl calix[6]arene matrix and its application for electrocatalytic reduction of H₂O₂

Jahan Bakhsh Raof^{a,*}, Reza Ojani^a, Ehteram Hasheminejad^a, Sahar Rashid-Nadimi^b

^a Electroanalytical Chemistry Research Laboratory, Department of Analytical Chemistry, Faculty of Chemistry, Mazandaran University, 3rd Kilometer of Air Force Road, 47416-95447 Babolsar, Iran

^b Department of Renewable Energy, Faculty of Advanced Science and Technology, University of Isfahan, 81746-73441 Isfahan, Iran

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ABSTRACT

The silver nanoparticles were prepared on the glassy carbon (GC) electrode, modified with *p*-iso propyl calix[6]arene, by preconcentration of silver ions in open circuit potential and followed by electrochemical reduction of silver ions. The stepwise fabrication process of Ag nanoparticles was characterized by scanning electron microscopy and electrochemical impedance spectroscopy. The prepared Ag nanoparticles were deposited with an average size of 70 nm and a homogeneous distribution on the surface of electrode. The observed results indicated that the presence of calixarene layer on the electrode surface can control the particle size and prevent the agglomeration and electrochemical deposition is a promising technique for preparation of nanoparticles due to its easy-to-use procedure and low cost of implementation. Cyclic voltammetry experiments showed that Ag nanoparticles had a good catalytic ability for the reduction of hydrogen peroxide (H₂O₂). The effects of *p*-isopropyl calix[6]arene concentration, applied potential for reduction of Ag⁺, number of calixarene layers and pH value on the electrocatalytic ability of Ag nanoparticles were investigated. The present modified electrode exhibited a linear range from 5.0×10^{-5} to 6.5×10^{-3} M and a detection limit 2.7×10^{-5} M of H₂O₂ (S/N = 3) using amperometric method.

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1. Introduction

In recent year, there has been considerable interest in detection of hydrogen peroxide because of its wide and varied applications. For example, H₂O₂ is useful for the synthesis of various organic compounds, food production, sterilization, clinical and pharmaceutical applications [1,2]. H₂O₂ is also used as an oxidant for liquid-based fuel cells [3,4] and has emerged as an important by-product of enzymatic reactions in the field of biosensing [5–8].

H₂O₂ determination can be carried out using several analytical techniques such as titrimetry [9], spectrophotometry [10–12], fluorometry [13–15], chemiluminescence [16–18], and chromatography [19–21]. However, electrochemical methods have emerged as preferable, owing to their relatively low cost, simplicity, efficiency and high sensitivity [22–24]. Hence, efficient and reliable materials with extraordinary electrocatalytic activities have been the goal for research groups to fabricate novel sensors for H₂O₂ detection. Until now, different materials such as noble metals, macro cycle complex of transition metals, carbon nanotubes and

enzymes have been used to modify electrodes for the detection of H₂O₂ [1,24].

Among different materials, metal nanoparticles have attracted much attention due to their unique properties and wide varieties of potential applications in various areas including catalysis, magnetic materials, information storage, microelectronics, and optoelectronics [25,26]. Several electrodes modified with metal nanoparticles such as Pt nanoparticles [27–29], Au nanoparticles [30–32], Pd nanoparticles [33] and Ag nanoparticles [34] have been widely used to prepare H₂O₂ sensor due to their large specific surface area, excellent conductivity and extraordinary electrocatalytic activities. As typical nanomaterials, Ag nanoparticles have been employed to modify electrode surfaces because of their potential applications. For example, Ag nanoparticle-attached surfaces can be used to prepare a surface-enhanced Raman scattering-active substrate [35], an ammonia sensor [36], a glucose sensor [34] and a hydrogen peroxide sensor [34,37]. Recent studies have shown that the Ag nanoparticles possess good catalytic activity for H₂O₂ [38].

In recent years, new efforts have been emphasized on the fabrication of H₂O₂ sensors by templated electrodeposition of nanostructures for enhanced oxidation/reduction and sensitive detection of H₂O₂ [39]. Calix[*n*]arenes are well-known cup-shaped cyclic oligomers, made up of phenol units. These compounds have

* Corresponding author. Tel.: +98 112 5342392; fax: +98 112 5342350.
E-mail address: j.raoof@umz.ac.ir (J.B. Raof).

hydrophobic cavities to hold smaller molecules or ions and belong to the class of cavitands known in host-guest chemistry [40,41]. Among various calix[*n*]arenes, *p*-isopropyl calix[6]arene can possess a good coordination ability towards silver ions because of having hydroxyl groups and a cavity with convenient size. Therefore, we attempted to utilize this compound as a template to fabricate the Ag nanoparticles on the surface of electrode.

In this paper, a new simple and direct strategy for the preparation of silver nanoparticles on a GC electrode, modified with *p*-isopropyl calix[6]arene, was described and the electrocatalytic activity of Ag nanoparticles towards H₂O₂ reduction was investigated. Scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterize the surface of resulting electrodes. The effects of *p*-isopropyl calix[6]arene concentration, applied potential for reduction of Ag⁺, number of calixarene layers and the pH value of phosphate buffer solution (PBS) on the catalytic activity of produced Ag nanoparticles were also discussed.

2. Experimental

2.1. Materials

p-Isopropyl calix[6]arene was obtained from Merck. AgNO₃ and hydrogen peroxide (35%) were purchased from Fluka. PBS was prepared by mixing 1.0 M stock solutions of NaH₂PO₄ and Na₂HPO₄ with certain ratio. All other chemicals were of analytical grade and used without further purification. Double-distilled water was used throughout this experiment.

2.2. Apparatus

Electrochemical measurements were performed using a potentiostat and galvanostat (model Autolab, PGSTAT30, Eco chemie, Netherlands) connected to a Pentium IV personal computer (FRA software for impedance spectroscopy and GPES software for voltammetry and amperometry were used). A conventional three-electrode system was used with a modified *n*-Ag/GC electrode as a working electrode, a platinum wire as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All experiments were performed at room temperature (25 ± 2 °C). Electrolyte solutions were deoxygenated by purging pure nitrogen (99.999%) for 10 min prior to electrochemical experiments.

Faradic impedance measurements were performed in the presence of a 1.0 mM K₃Fe(CN)₆/K₄Fe(CN)₆ (1:1)-mixture as a redox-probe, containing 0.1 M KCl, using an alternating current voltage of 5 mV. Impedance measurements were performed at an open circuit voltage (OCV) of 0.21 V.

The nanostructures and morphology of synthesized nanoparticles were studied by Philips XL 30 scanning electron microscope (SEM).

2.3. Preparation of Ag nanoparticles/glassy carbon electrode (*n*-Ag/GCE)

The GC electrode was polished carefully with 0.3 μm alumina slurry then washed and sonicated in double-distilled water and ethanol, each for a few minutes, and dried in air. Then 1 μL *p*-isopropyl calix[6]arene solution (0.01 M in THF solvent) directly dropped onto the surface of the cleaned GC electrode and dried at room temperature. Obtained electrode was immersed in 1.0 mM AgNO₃ solution containing tetra-ethyl ammonium hydroxide (pH = 7.0) for 10 min. Continuously, the accumulated silver ions, electrochemically were reduced for 25 s at −0.3 V vs. SCE. Processes of dropping, immersing and electrochemical reduction of Ag⁺ were carried out for 5 times because the electrode modified with five

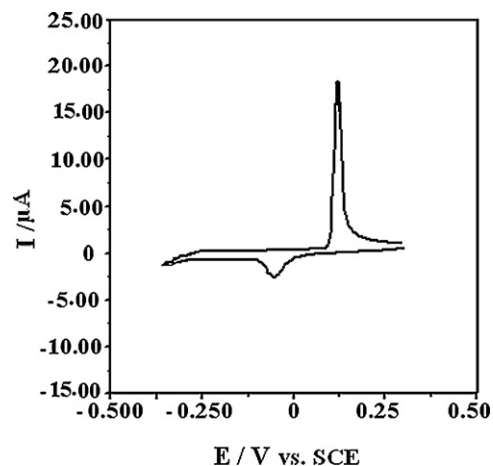


Fig. 1. Cyclic voltammogram of Ag nanoparticles on the modified GCE in 0.1 M PBS (pH = 7.0) at scan rate of potential 50 mV s⁻¹.

layers of calixarene showed the best response towards the reduction of H₂O₂. Finally, the calixarene layer was removed from the surface of electrode by immersing the modified electrode in stirred pure THF for 10 min.

3. Results and discussion

3.1. Characterization of *n*-Ag/GCE

Direct evidence for the formation of Ag nanoparticles on the surface of modified electrode can be obtained from a close inspection of the oxidation–reduction behavior of these nanoparticles. Fig. 1 showed cyclic voltammogram of the Ag nanoparticles-modified GC electrode after the potentiostatic step in 0.1 M PBS at pH 7.0. The *n*-Ag/GC electrode exhibited a clear anodic peak with a peak potential of +0.12 V vs. SCE, which was the characteristic oxidation peak of Ag nanoparticles and a small reduction peak appeared at potential of about −0.05 V vs. SCE, which was associated with the reduction of Ag⁺ cations.

The surface morphology and distribution of metal nanoparticles on the support surface can be further exploited by scanning electron microscopy. Fig. 2 showed SEM images of the electrode surface obtained during different steps of modifying process. Fig. 2A indicated the morphology of bare GC electrode surface after polishing. As shown in this image, there are some defects on the electrode surface that obtained during polishing the surface of electrode. Fig. 2B showed the structure of the calixarene layer after deposition of Ag on the electrode. Fig. 2C also, depicted the structure of the surface of *n*-Ag/GCE after resolution of calixarene layer. As shown in this image, Ag nanoparticles with an average size of 70 nm were deposited on the surface of electrode. It can be seen that the Ag nanoparticles was exhibiting a homogeneous distribution on the electrode surface. In contrast, the adsorbed Ag⁺ on the bare GCE formed large Ag blocks with irregular shapes in the absence of the calixarene film (Fig. 2D). These results implied that in the absence of calixarene film, Ag atoms produced from the electroreduction of Ag⁺ grew preferentially on deposited Ag nuclei to form large blocks, while the calixarene acted as a template on the electrode surface to greatly increase quantity of the Ag nanoparticles and decrease their dimension and also prevented from aggregation of the Ag atoms into the large blocks. Therefore, the calixarene film could control the size, quantity and distribution of the produced Ag nanoparticles.

EIS was applied to monitor the procedure in preparing modified electrodes, which could provide significant information at

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