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Facile synthesis of silver nanostructures by using various deposition potential and time: A nonenzymetic sensor for hydrogen peroxide

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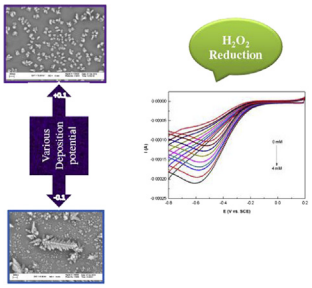
HIGHLIGHTS

- Silver nanostructures (AgNS) have been fabricated using electrodeposition ITO.
- AgNS with different morphology and electrochemical properties obtained.
- AgNS exhibits good electrocatalytic activity for reduction of H_2O_2.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanostructures have been successfully fabricated by using electrodeposition method onto indiumtinoxide (ITO) substrate. Scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and ultraviolet–visible spectroscopy (UV–Vis) techniques were employed for characterization of silver nanostructures. The results show nanostructures with different morphology and electrochemical properties can be obtained by various deposition potentials and times. Electrochemical behavior of the nanostructures has been studied by using cyclic voltammetry. Silver nanostructures exhibits good electrocatalytic activity towards the reduction of H_2O_2. The presented electrode can be employed as sensing element for hydrogen peroxide.

1. Introduction

Recently, noble metal nanostructures have been received considerable attention, because of their unique mechanical, electrical, optical, catalytic and magnetic properties that due to their size-shape dependent properties and quantum size effects [1–4]. Among noble metal nanostructures, silver has been a subject of intensive researches because it possess high electrical and thermal conductivity, excellent biocompatibility, versatile physical and chemical properties, strong antibacterial effects for a vast range of organisms (e.g., viruses, bacteria, fungi), valuable optical properties (surface plasmon resonance (SPR), sharp extinction bands, high ratio of scattering to extinction) and relatively low cost in comparison with gold or platinum [2,5–10]. These properties allow silver nanostructures (AgNS) to be used in the broad applications such as electronics [11], optics [12,13], catalyst [14,15], gas sensing [16,17], chemical and biological sensing [18–21], various imaging and detection modes (e.g. fluorescence [22], colorimetric [23], surface-enhanced Raman scattering (SERS) [24,25], medical devices and textile industry [26–28]. Furthermore, AgNS can also be used in electrochemistry because of some advantages such as non-toxicity, ability to adsorb inorganic ions and organic substances,

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wide analytical range and availability. Actually, using of nanostructures arrays in electrochemistry and nanoelectrodes, is one of the very interesting research subject. It is because of the advantages that are associated with these type of electrodes such as large effective sensor surface area, considerable mass transport, high catalytic activity and use a small amount of material [29–33]. So, AgNS can be very good candidates in various types of electrochemical sensors [34,35].

Many synthesis methods in both chemical and physical categories including wet chemical [36], polyol process [37], seed-mediated growth [38], photochemical [39], sonochemical [40], electrochemical [41], sputtering [42] and laser ablation [43] have been reported for preparing of various silver nanostructures, such as spherical [44], nanodisks [45], nanowires [46], flower-like nanoarrayes [47], nanocubes [48], nanorods [49], nanofilms [50], nanodendrites [51] and nanoprisms [52]. However, most of chemical methods have some disadvantages like using organic solvents, toxic reducing agents, and additional reagents like surfactant or soft template, by-products, impurities and systematic conditions such as heating, stirring and lighting. Many of the resulted nanostructures are colloidal and powder form that can be aggregated. Solvents and reducing agents can effect on physical and morphological characteristics of manufactured silver nanoparticles. Compared with the chemical methods, physical methods are often contamination free, but they need special conditions like high temperature or low pressure environment. In addition they are expensive and time consuming procedures.

Electrochemical methods are preferable to other methods due to the good control of size, shape and morphology of the nanostructures with high purity. Electrodeposition is one of the electrochemical methods in which nanostructures are directly electrodeposited onto a substrate for large-scale fabrication. It has following advantages: fast, simple, one-step, low equipment and production cost, environmentally friendly, avoiding the use of vacuum systems or high temperatures processes and easier control of shape and size [53,54].

Nowadays, considerable attention has been paid to detection of hydrogen peroxide (H_2O_2), owing to its wide applications in food, pharmaceutical, clinical and environmental analyses. It is a strong oxidant and also a final product of various enzymatic reactions and its detection can be used as direct indicator for the progress of reactions. Electrochemical methods because of their cheap cost, high efficiency, high accuracy and consistency, simplicity and fast analysis are used for detection of H_2O_2, mostly. Several studies have been reported catalytic activity of AgNS through H_2O_2 electrochemical determination [55–57].

In this paper, electrodeposition as a simple and direct strategy for the preparation of silver nanostructues onto ITO substrate (AgNS/ITO) was described. Scanning electron microscopy (SEM), UV–Vis spectrophotometry and electrochemical impedance spectroscopy (EIS) were used to characterize the surface of electrodes. Electrocatalytic activity of Ag nanostructures towards H_2O_2 reduction was studied. Also, the effects of deposition potential time on the morphology and electrochemical activity of fabricated electrode (AgNS/ITO) were investigated.

2. Experimental

2.1. Chemicals

$AgNO_3$, KNO_3 (99%), $K_4Fe(CN)_6$, $K_3Fe(CN)_6$ (99.5%) and H_2O_2 (30%, v/v aqueous solution) were purchased from Merck and were of analytical grade reagent. ITO thin film coated onto an ordinary glass substrate (1 cm × 2 cm, 30 Ω per square, SAIRAN company). Dilute solutions of H_2O_2 were freshly prepared daily. Phosphate buffer solution (PBS, pH 7.0, 0.1 M) as supporting electrolyte was prepared using KH_2PO_4 and K_2HPO_4. All aqueous solutions were prepared with doubly distilled water. All experiments were performed at room temperature, approximately 25 °C.

2.2. Instrumentation

Cyclic voltammetry (CV) was performed with a Metrohm Computrace voltammetric analyzer model 797VA. A conventional three-electrode system was used with a saturated calomel electrode (SCE) as reference, a platinum wire as auxiliary and silver nanostructures coated onto ITO (AgNS/ITO) used as working electrodes. A digital pH/mV/Ion meter was applied for the preparation of the buffer solutions, which were used as the supporting electrolyte in voltammetric experiments. Surface morphology and distribution of particles were studied via LEO 1430VP scanning electron microscopy (SEM), using an accelerating voltage of 15 kV. UV–Vis absorption spectrums were obtained using a UV-1650PC spectrophotometer (Shimaduz Co., Japan). A microAutolab electrochemical analysis system was used for the electrochemical impedance spectroscopy (EIS).

2.3. Preparation of silver nanostructures

The ITO electrodes were cleaned prior to use by rinsing with methanol, deionized water and acetone and followed by drying for 10 min in a furnace at 70 °C in air. The electrodeposition of silver nanostructures was performed in solution containing 1 mM $AgNO_3$ and 0.1 M KNO_3 (vs. SCE as reference electrode) at the surface of ITO as working electrode. For observing the effect of potential and time of deposition on the morphology of silver nanostructures, two different deposition time (60 s and 120 s) and deposition potential (−0.1 V and +0.1 V) were used to fabricate the silver nanostructures.

3. Results and discussion

3.1. Characterization of AgNS

3.1.1. SEM results

The effect of time and potential of deposition were investigated on morphology of silver nanoparticles. To study the surface morphology of the AgNS, scanning electron microscopy (SEM) has been utilized. Scanning electron micrographs of the silver nanostructures at the surface of ITO in two various deposition potentials (−0.1 and +0.1 V) at the deposition time 60 s are shown in Fig. 1. The size of fabricated Ag nanoparticles in E = −0.1 V have distribution size between 40 and 80 nm (See Fig. 1A). In more positive potential, E = +0.1, the agglomeration increase and some flower-like nanostructures have been produced (See Fig. 1B).

As can be seen, the deposition potential has a significant effect on the size and morphology of silver nanostructures. Nucleation rate is higher at less positive potential then the surface of substrate coated by silver nanoparticles homogeneously. But in more positive potentials, nucleation rate is slower and of silver nanoparticles can be aggregated [58].

Fig. 2 exhibits the SEM images of AgNS at the surface of ITO in deposition potential −0.1 V and deposition time 120 s. Comparing the images of AgNS at different deposition times (Figs. 1A and 2) show that with increasing the deposition time, silver nanoparticle are becoming more associate to each other and the mean size increased then interparticle distance became wider and the distribution onto the surface are changed [58]. The noticeable nanostructures are related to Fig. 2, in which dendritic morphological forms were formed. In reality, Diffusion-limited aggregation (DLA)

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