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Electrodeposited Silver Nanostructures: A Non-Enzymatic Sensor for Hydrogen Peroxide

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Abstract**—**Silver nanostructures have been successfully fabricated by using electrodeposition method onto indium-tin-oxide (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 the 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.

Keywords**—**Electrochemical sensor, electrodeposition, hydrogen peroxide, silver nanostructures.

I. 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]. Among noble metal nanostructures, silver have been a subject of intensive researches because they 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]-[7]. These properties allow silver nanostructures (AgNS) to be used in the broad applications such as electronics [8], optics [9], catalyst [10], gas sensing [11], chemical and biological sensing [12], various imaging and detection modes (e.g. fluorescence [13], colorimetric [14], surface-enhanced Raman scattering (SERS) [15], medical devices and textile industry [16]. Furthermore, AgNS can also be used in electrochemistry because of some advantages such as nontoxicity, ability to adsorb inorganic ions and organic substances, wide analytical range and availability. Using of nanostructures arrays in electrochemistry and nanoelectrodes is one of the very interesting areas of research because of the advantages that are associated with these types of electrodes such as large effective sensor surface area, considerable mass transport, high catalytic activity and use a small amount of material [17]. So, AgNS can be very good candidates in various types of electrochemical sensors [18].

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 [19].

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 a direct indicator for the progress of reactions. Several studies have been reported catalytic activity of AgNS through H_2O_2 electrochemical determination. 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 [20]- [22].

In this paper, electrodeposition as a simple and direct strategy for the preparation of silver nanostructures 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 applied potential for reduction of Ag^+ and time of applying potential on the morphology and electrochemical activity of fabricated electrodes (AgNS/ITO) were investigated.

II. Experimental

A. Materials and Instrument

$AgNO_3$, 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-reagent grade. Indium tin oxide thin film coated onto an ordinary glass substrate (1 cm×2 cm, 30 Ω per square, SAIRAN company). Cyclic voltammetry was performed with a Metrohm Computrace voltammetric analyzer model 797VA. A conventional three-electrode system was used with a saturated calomel electrode (SCE) as a reference, platinum wire as auxiliary and silver nanostructures

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coated onto ITO (AgNS/ITO) used as working electrodes. 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.

B. Procedure: 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 a solution containing 1 mM $AgNO_3$ and 0.1 M KNO_3 (vs. SCE as a reference electrode) at the surface of ITO as working electrode. For observing the effect of the potential and the 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.

III. Results and Discussion

A. Characterization of AgNS

1.SEM Results

To study the surface morphology of the AgNS, scanning electron microscopy (SEM) has been utilized. The effect of time and potential of electrodeposition were investigated on the morphology of silver nanoparticles. 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 40-80 nm. But in more positive potential E= +0.1 agglomeration happens more and some flower-like nanostructures have been produced.

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 than the surface of the substrate coated by silver nanoparticles homogeneously. But in more positive potentials, nucleation rate is slower and of silver nanoparticles can be aggregated [23].

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. 1 (a) and 2) show that with increasing the deposition time, silver nanoparticles are becoming more associate to each other, the mean size increased, interparticle distance became wider and type of distribution onto the surface are changed [23]. The noticeable nanostructures are related to Fig. 2, in which dendritic morphological forms were formed. In reality, Diffusion-limited aggregation (DLA) model is used to explain the growth mechanism of Ag dendritic structure. This model has expressed that the dendritic growth occurs by sticking of particles together with a random path to a selected seed in contact allowing the particles to form a growing structure and growing mostly happen at the tips and stems of branches that formed firstly [24].

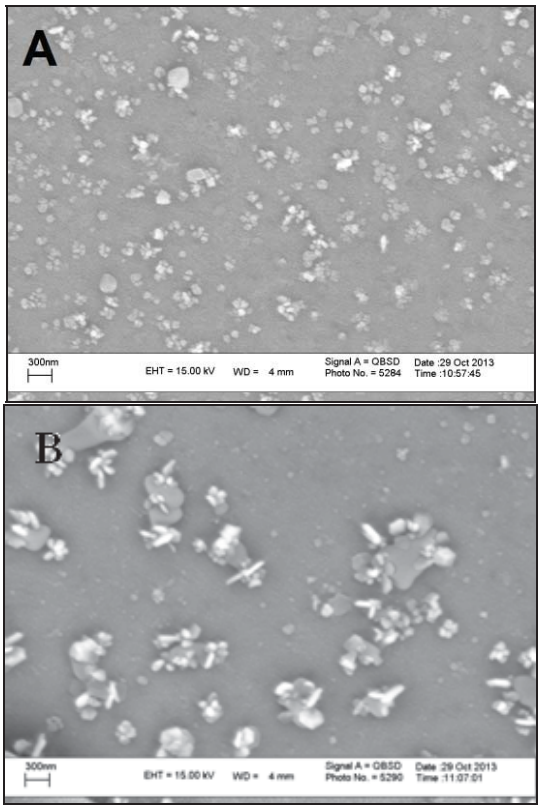


Fig. 1 SEM images of silver nanostructures that prepared at a deposition time 60 s and different deposition potentials: (a) -0.1 V (b) +0.1 V

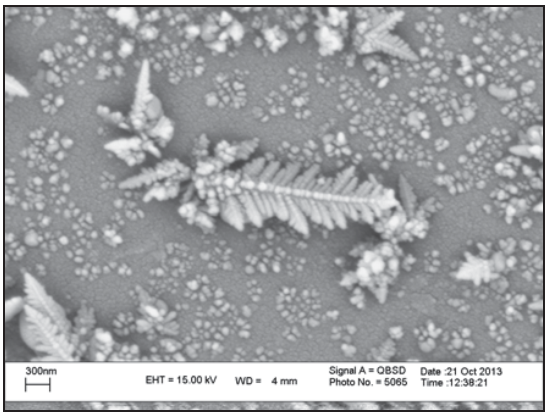
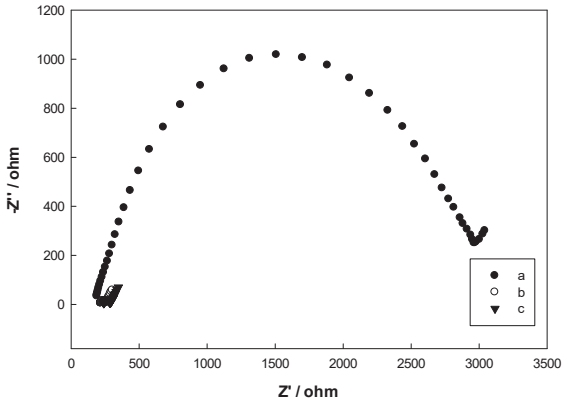


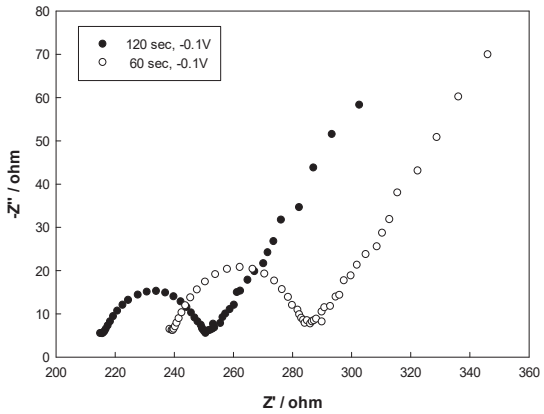
Fig. 2 SEM image of silver nanostructures that prepared at a deposition time 120 s and deposition potential -0.1 V

It is found that the morphology of silver structures electrodeposited onto an ITO surface is highly dependent on the deposition potential and deposition time. It attributes to effecting of several experimental parameters such as potential, deposition time, electrode substrate and so on that can

modulate the final composition and morphology of the deposits [25].



(a)



(b)

Fig. 3 Nyquist plots for bare ITO (a), silver nanostructures electrodeposited at -0.1Volt in various deposition times (b) 60 s and 120 s, in 5 mM $Fe(CN)^{3-/4-}$ containing 0.1 M KNO_3. The frequency ranged from 10^{-1} - 10^4 Hz

2.Electrochemical Impedance Spectroscopy Results

Electrochemical impedance spectroscopy (EIS) was employed to investigate the impedance changes of the electrode surface due to electrodeposition of silver nanostructures at the surface of ITO substrates. Fig. 4 shows the Nyquist plots of $K_3Fe(CN)_6/K_4Fe(CN)_6$ at the surface of ITO coated silver nanostructures prepared in different deposition times. In these studies, high-frequency zone, which appears as a near semicircle plot, can be ascribed to the kinetic limitations (R_{ct}) of the electrochemical reaction. On the other hand, the linear behavior of Z_{Im} versus Z_{Re} in a low-frequency region is characteristic of a diffusion-controlled electrode process at the surface of ITO coated silver nanostructures. As can be seen in Fig. 4 Nyquist plot is shown a semicircle with a very large diameter for the bare ITO (Fig. 3 (a)), but by electrodepositing of silver onto the surface of ITO, the diameter of the semicircle was significantly reduced (Figs. 3 (a) and (b)), suggesting that silver can form high electron conduction pathways and makes the electron transfer easier. Furthermore, results indicated that with increasing electrodeposition time, more amount of silver was deposited onto the substrate, so effectively enhanced the conductivity of the surface [26].

3.Cyclic Voltammetry Studies

The effects of several parameters such as deposition time and potential on the voltammetric response of AgNS were investigated.

(i) The effect of deposition time: Cyclic voltammograms of AgNS deposited onto ITO at deposition potential +0.1 V and different deposition time (a) 60 s (b) 120 s in buffer solution pH 3 are shown in Fig. 4 Oxidation peak at 0.7 V is related to electrooxidation of AgNS and reduction peak at 0.1 V attributed to consequent reduction of Ag^+ to Ag [27].

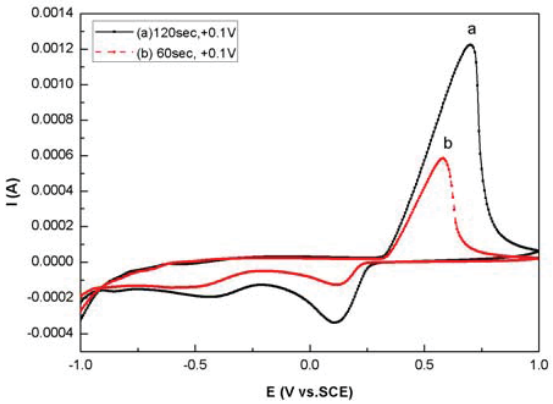


Fig. 4 Cyclic voltammograms of silver nanostructures prepared at deposition potential +0.1V and different deposition times (a) 120 s (b) 60 s, in 0.1 M phosphate buffer solution pH 3, scan rate 0.05 V s^{-1}

Also, it can be seen, by increasing the deposition time, the oxidation and reduction peak currents increased due to deposition of more amount of silver onto substrate.

(ii) The effect of deposition potential. Fig. 5 shows cyclic voltammograms for oxidation and reduction of deposited silver nanostructures on ITO in phosphate buffer solution pH 3. It is obvious that by increasing the deposition potential, both anodic and cathodic current are increased. It can be concluded that more amount of deposited silver onto surface of ITO during the electrodeposition procedure. The results have good agreement with SEM images.

B. Investigation of Hydrogen Peroxide Reduction at the Surface of AgNS / ITO Electrode

For evaluating the electrocatalytic potential of the prepared AgNS/ITO electrode, it has been employed as catalysts toward the electro-reduction of hydrogen peroxide. The behavior of four types of silver nanostructures was investigated by using cyclic voltammetry in the phosphate buffer solution pH 7 containing 2 mM H_2O_2.

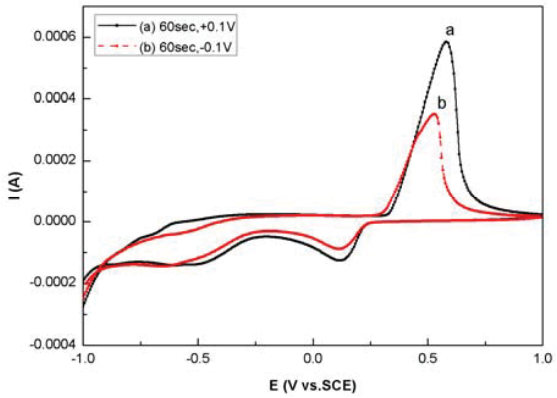


Fig. 5 Cyclic voltammograms of AgNS prepared at deposition time 60 s and different deposition potentials (a) +0.1 V (b) -0.1 V, in 0.1 M phosphate buffer solution pH 3, scan rate 0.05 V s^{-1}

The best catalytic current was obtained on the surface of silver nanostructure that was prepared at 60 second and -0.1V. This result is in good agreement with the SEM images in that a great number of small silver nanoparticles were deposited onto the ITO homogeneously and show larger surface area. It can be provided a more active area for the reduction of H_2O_2. So, the AgNS that had prepared at 60 s and -0.1 V in the electrodeposition procedure was chosen as the AgNS/ITO electrode for further studies.

1.The Effect of Concentration of Hydrogen Peroxide

The electrocatalytic activities towards H_2O_2 reduction were examined by changing the H_2O_2 concentration. Cyclic voltammetry in phosphate buffer solution in the presence of H_2O_2 with different concentrations (from 0 to 4 mM) was performed. Results are illustrated in Fig. 6. It is found that the peak current increased gradually by increasing the concentration of H_2O_2.

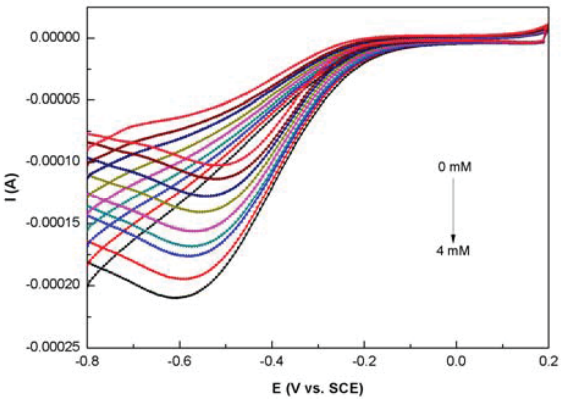


Fig. 6 Cyclic voltammograms of AgNS/ITO electrode in 0.1M phosphate buffer solution pH 7 in the presence of H_2O_2 with different concentrations (from the top: 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 mM), scan rate 0.05 V s^{-1}

IV. Conclusion

In summary, we have successfully fabricated various silver nanostructures at the surface of ITO through a facile, simple and efficient method. Various characterization techniques such as scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS) that were used, exhibited the effect of deposition potential and the deposition time on the final structure and morphology of silver nanostructures. We also demonstrate the successful application of these nanostructures in electrochemical detection of H_2O_2 in phosphate buffer solution (PBS).

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