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Controlling of morphology and electrocatalytic properties of cobalt oxide nanostructures prepared by potentiodynamic deposition method

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ABSTRACT

Electrodeposited cobalt oxide nanostructures were prepared by Repetitive Triangular Potential Scans (RTPS) as a simple, remarkably fast and scalable potentiodynamic method. Electrochemical deposition of cobalt oxide nanostructures onto GC electrode was performed from aqueous $Co(NO_3)_2$, (pH 6) solution using cyclic voltammetry method. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to characterize the morphology of fabricated nanostructures. The evaluation of electrochemical properties of deposited films was performed using cyclic voltametry (CV) and impedance spectroscopy (IS) techniques. The analysis of the experimental data clearly showed that the variations of potential scanning ranges during deposition process have drastic effects on the geometry, chemical structure and particle size of cobalt oxide nanoparticles. In addition, the electrochemical and electrocatalytic properties of prepared nanostructures can be controlled through applying different potential windows in electrodeposition process. The imaging and voltammetric studies suggested to the existence of at least three different shapes of cobalt-oxide nanostructures in various potential windows applied for electrodeposition. With enlarging the applied potential window, the spherical-like cobalt oxide nanoparticles with particles sizes about 30–50 nm changed to the grain-like structures (30 nm × 80 nm) and then to the worm-like cobalt oxide nanostructures with 30 nm diameter and 200–400 nm in length. Furthermore, the roughness of the prepared nanostructures increased with increasing positive potential window. The GC electrodes modified with cobalt oxide nanostructures shows excellent electrocatalytic activity toward H_2O_2 and As (III) oxidation. The electrocatalytic activity of cobalt oxide nanostructures prepared at more positive potential window toward hydrogen peroxide oxidation was increased, while for As(III) oxidation the electrocatalytic activity decreased with enlarging positive potential window. Therefore, with changing the experimental condition in electrodeposition process the electrocatalytic properties of the cobalt oxide nanostructures toward analytes is selectable and controllable.

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1. Introduction

Conductive transition-metal oxides form important and diverse materials that have attracted much attention in many fields of technological interest because of their outstanding electronic, optical, magnetic, and catalytic properties. The development of metal oxide nanocrystals has been intensively pursued because of their useful applications in catalysis, energy storage, magnetic data storage, sensors and ferrofluids [1–5]. Among these, cobalt and cobalt oxide materials and nanomaterials have attracted a great interest in view of their various applications in scientific and technological fields.

Cobalt and cobalt-oxide have been employed in the production of batteries and supercapacitors [6–8], electrochromic devices [9–11] magnetic and other devices [12,13]. Also cobalt oxide is considered to be an important functional material, and has been widely used in heterogeneous catalysts [14,15], sensors and biosensors [16–20]. Several methods have been developed for the synthesis of cobalt oxide films and nanostructures. Chemical Vapor Deposition (CVD) [21], Physical Vapor Deposition (PVD) [22], Spray Pyrolysis [23], Sol-gel Process [24], Wet Chemical Method [25], Atomic Layer Deposition (ALD) [26] and Electrodeposition [27–29] are some of the extended methods. Among the various approaches for the fabricating of such nanostructures, the electrodeposition technique has been proved as an extremely versatile and simple method. On the other hand, in fabrication of such functional materials and devices, it is sometimes important to assemble the nanoparticles onto solid substrates. Charged polymers and other functional polymers have

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been employed to anchor the nanoparticles as a layer onto various substrates, including glasses, semiconductors, metals, and carbons. Then the electrodeposition technique is interested in fabrication of robust multilayered nanostructures on the used substrate. It has been shown recently that the electrodeposition is a useful technique for growing cobalt and cobalt oxide nanostructures for different application [30–32]. Various electrodeposition methods including Conventional Direct Current Deposition [23], Pulse Electro Deposition [33], and potentiodynamic method [34] have been used to produce cobalt and cobalt oxide nanostructures with different size and morphology. It is well known that the behavior of nano-phase materials strongly depend on the morphology and grain size of the particles, which are key factors in their ultimate performances and applications. Also physical and chemical parameters and compositions of the electrolysis solution such as additives concentration [35], temperature and pH of solution [34,36], current on and off time [21,37] and current density [22,38] can affect the grain size and surface morphology of the deposits. As a useful method, pulsed and pulse reverse electrodeposition were used to grow metallic cobalt nanoparticles with controlled size and shape [21,23,39,40]. The dependence of morphology, catalytic activity and electrochemical behavior of constructed cobalt oxide film in potentiostatic and potentiodynamic conditions have been investigated [24,41]. In this work, we present a simple and inexpensive one-step template-less process using repetitive Triangular Potential Scans to grow cobalt oxide nanostructures with controlled size and shape onto glassy carbon electrode. This work aimed to study the shapes, morphologies and electrocatalytic activities of cobalt oxide nanostructures fabricated in various potentiodynamic conditions. The electrocatalytic activities of prepared cobalt oxide nanostructures toward oxidation of arsenate and hydrogen peroxide under different conditions were evaluated.

2. Experimental

2.1. Reagents

Solutions were prepared from analytical-reagent grade chemicals without further purification. Cobalt nitrate, sodium hydroxide and hydrogen peroxide were purchased from Merck. The phosphate buffer solutions (PBS) (0.1 M) were prepared from H_3PO_4, KH_2PO_4 and K_2HPO_4. The pHs of the buffer solutions were adjusted with HCl and KOH solutions.

2.2. Apparatus

A μ-Autolab (Eco Chemie Ultrecht, The Netherlands) potentiostat/galvanostat monitored by GPES software was used in electrochemical experiments. Cyclic voltammetry (CV) was performed in a three-electrode cell using glassy carbon (GC) as working electrode (WE), Ag/AgCl (sat. KCl) as a reference electrode (RE) and platinum wire as counter electrode (CE). Voltammetry on electrodes modified with cobalt oxide nanostructures was done in buffers that contained no cobalt salt. All experiments were carried out at ambient temperature of $20 \pm 1\,^\circ$C. The surface morphology of modified electrodes was studied with a Vega-Tesacn electron microscope and NT-MDT atomic force microscope (AFM).

2.3. Preparation of electrodeposited cobalt oxides nanostructures

Glassy carbon electrode (2 mm diameter) was carefully polished with alumina on a polishing cloth. The electrode was sonicated in ethanol in order to remove the adsorbed particles. Cyclic voltammetry (Repetitive Triangular Potential Scans (RTPS)) was used as potentiodynamic method in deposition of cobalt oxide nanostructures film. Glassy carbon electrodes were subjected to repetitive
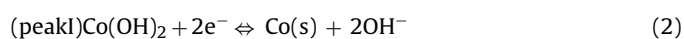
triangular potential scans (RTPS) in 10 mM of cobalt(II) nitrate solution (between 0.0 V and −1.1 V) at $\upsilon = 100\,mV\,s^{-1}$ (sample 1). The other depositions were carried out by expanding applied potential range to a more positive value. Potential ranges of 0.5 V to −1.1 V and 1.2 V to −1.1 V were also used in preparation of second and third samples of cobalt oxide nanostructures denoted hereafter as samples 2 and 3, respectively. The glassy carbon/cobalt oxide electrode (GC/Co-Oxide electrode) was eventually washed with double distilled water and stored at ambient temperature (25 °C) before being used in experiments.

3. Results and discussion

3.1. Preparation of cobalt oxide nanostructures

Applied potential conditions during the electrodeposition process has significant role in nucleation and growth of nanoparticles [40,42,43]. Although potentiodynamic method frequently used to fabricate different nanostructures, the influence of potential range on deposition is rarely studied [27,33,44]. Based on purbaix diagram for cobalt, only at positive potentials (>1.2 V), Co^{2+} can be oxidized to higher valent oxides. At more positive potentials and in medium pH values, the high valance Co (III, IV) are partially stable [45]. It is known that the nucleation process is deeply depended to the applied potentials. The nucleation under negative potentials starts via metallic cobalt nucleus. On the other hand, nucleation under positive potentials takes place by formation of cobalt hydroxide and cobalt oxide species. Therefore, during the potential cycling between E_s (starting potential) and E_r (reversing potential), different spices of cobalt such as Co, Co(OH)$_2$, Co(III) and Co(IV) are involved in the electrochemical processes which have significant role in the nucleation and therefore in growing process [46].

Here in order to studying the dependence of composition and morphology of deposited species to applying potentials, the electrodeposition was carried out under three different potential windows (0.0 V to −1.1 V, +0.5 to −1.1 V and +1.2 to −1.1 V). Fig. 1 shows triangular potential scans at these three potential ranges. Fig. 1a shows the cyclic voltammogram of GC electrode in 10 mM Co(NO$_3$)$_2$ solution (pH 6) at potential range of E_s = 0.0 V to E_r = −1.10 V (sample 1). As can be seen, the rising cathodic peak is observed at −1.05 V due to reduction of Co^{2+} ions that is related to three-dimensional nucleation and growth of cobalt at glassy carbon electrode (Co^{2+} to Co) [39,40,47]. At reverse scan, a small anodic peak is shown next to -0.24 V that corresponds to dissolution of deposited cobalt (Co to Co^{2+}). In order to evaluate the effect of the potential sweep range during the electrodeposition of cobalt, in the second experiment the E_r changed to 0.5 V (sample 2). As illustrated in Fig. 1b, the new peak was observed at 0.5 V due to oxidation of Co (II) to Co (III). Finally, in the last experiment the starting potential was changed to 1.2 V and cyclic voltammetry was performed in the potential range of E_s = 1.2 V to E_r = −1.10 V (sample 3). As can be seen in Fig. 1c, two anodic peaks were observed at potential range between 0.7 V and 1.2 V which attributed to Co (II) to Co (III) and Co (III) to Co (IV) oxidation processes. Repetitive potential scans (10 scan) was used to prepare cobalt oxide nanostructures (samples 1–3) onto glassy carbon electrode. As an example, repetitive cyclic voltammograms in 10 mM Co (NO$_3$)$_2$ (pH 6) is shown in Fig. 2. Growing the cobalt oxide nanostructures was indicated by increasing anodic (peaks III, IV) and cathodic (peak V) currents at about 0.75 V and 1.0 V corresponded to two electrochemical reactions. The following equations should be assigned the observed peaks in Fig. 2.

$$(peakI)\,Co^{2+} + 2e^- \Leftrightarrow Co(s) \tag{1}$$

$$(peakI)\,Co(OH)_2 + 2e^- \Leftrightarrow Co(s) + 2OH^- \tag{2}$$