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Electrochemical and Electrocatalytic Properties of Cobalt Oxide Nanoparticles

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The synthesis and characterization of cobalt oxide nanoparticles are reported. Cobalt oxide nanoparticles prepared by two ways. In first way cobalt chloride mixed with sodium carbonate, the obtained precipitate react in solid state reaction with oxalic and citric acid separately at about 70 ºC, then products oxidized by heating at different temperature from 400-700 ºC. In second way the cobalt chloride mixed with sodium hydroxide solutionat at 4 ºC and obtained precipitate heated as the first way from 400-600 ºC. The obtained cobalt oxide nanoparticles characterized by cyclic voltammetry and SEM techniques. The electrochemical behaviour of the cobalt oxide in carbon paste electrode (CPE) was studied by cyclic voltammetry. The cobalt oxide-CPE shows a pair of peaks with a surface-confined characteristic in a 0.5 M phosphate buffer and 0.5 M NaOH as supporting electrolyte. The cobalt oxide-CPE showed electrocatalytic activity toward oxidation of fructose. The kinetics of the catalytic reaction was investigated by using chronoamperometry.

Key Words: Electrocatalysis, Cobalt oxide nanoparticles, Fructose oxidation.

INTRODUCTION

Metal oxides represent an assorted and appealing class of materials which properties cover the entire range from metals to semiconductors and insulators and almost all aspects of material science and physics in areas including superconductivity and magnetism. Metal oxide systems have been the object of investigations by many authors during the last years[1-8]. Intensive research has been going on during the past several years to achieve selective sensors using metal oxides. In a few cases, a material giving a specific interaction with the molecule to be detected has been successfully used to design a highly selective gas sensor[9]. Advances in fabrication and materials technology have given simple, robust and low cost devices[10,11] using different

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metal oxides, such as CoO, ZnO, SnO_2, Fe_2O_3, *etc.* However, this type metal oxide often used as gas sensor, these sensors presents an inherent lack of selectivity, because the gas detection mechanism is rather unspecific and more or less any type of reducing or oxidizing gas is detected. Metal oxides are also important catalysts in a wide range of technical and electrochemical processes. Cobalt oxide (usually mixed with other metal oxides) in particular, has been shown to be an active catalyst for the hydrogenation of CO, towards ethylene and propylene[12], NO reduction[13], oxygen evolution process[14], complete benzene oxidation[15], NOx sensors[16], ozone monitoring[17], monitoring species like CO and NH_3[18], methane combustion catalysts[19], oxygen gas sensor[20] and CO sensing[21].

In this paper we describe the preparation and the characterization of cobalt oxide nanoparticles. Preliminary results on the electrochemical behaviour of cobalt oxide nanoparticles inserted in carbon paste electrode are reported. It is shown that with cobalt oxide nanoparticles inserted in carbon paste electrode, shows well-defined electrochemical behaviour for the oxidation of Fructose. The resulting cobalt oxide film prepared chemically in alkaline and inert (pH = 7) solutions was characterized by electrochemical and scanning electron microscopy (SEM) techniques.

EXPERIMENTAL

$CoCl_2$, NaOH, $NaNO_3$, KNO_3 and other chemicals were of analytical grade from Merck and Fructose was of analytical grade from Roth and used without further purification. A solution of 0.5 M phosphate buffer (pH = 7) or 0.5 M NaOH solution was used as supporting electrolyte.

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP-2063 electrochemical analysis system, Behpajooh, Iran). A conventional three-electrode cell was used at room temperature. A saturated calomel electrode and platinum wire were used as reference and auxiliary, respectively. SEM micrographs were taken with a Philips ESEM series XL 30 scanning electron microscope.

Preparation of cobalt oxide nanoparticles: Two series of experiments were employed to preparation of cobalt oxide. In a series of experiments cobalt chloride (0.1 M) solution was added on sodium carbonate (0.1 M) solution, the obtained precipitate filtered and dried. The cobalt carbonate was grind with solid oxalic acid or citric acid at 1:1 (mole ratio) in an agate mortar for 20 min. The mixture was then transferred into a test tube and heated at 70 ºC in a water bath for 1 h to assure that the reaction in solid state occurred completely and subsequently thermally decomposed at 400-600 ºC. In other series of experiments, cobalt chloride solution mixed with NaOH solution in 4 ºC. The obtained precipitate filtered and dried then thermally decomposed at 400-600 ºC. In both series of experiments, the precipitants and cobalt chloride concentrations varied. For study electrochemical properties of cobalt oxide nanoparticles, the cobalt oxide nanoparticles was mixed with 0.5 g graphite powder by ratio of 1:10 for 10 min and after adding two drops of paraffin oil to the mixture. The mixture filled a Teflon tube (with 3 mm I.d. and 10 cm length and length of nanoparticles composite in the tube was about 0.5 cm) After polishing the modified electrode; potential cycling for 30 cycles was accomplished. The cobalt oxide CPE showed stable electrochemical behaviour.

RESULTS AND DISCUSSION

Morphology of the nanoparticles: As mentioned in experimental section, the cobalt oxide nanoparticles was prepared by two different ways. According on SEM image obtained for nanoparticles from two ways, it seems that particles with second method was uniform and nanosized, but using solid state reaction between the cobalt carbonate and oxalic acid or citric acid produce large particle size. Fig. 1 shows the SEM image for particles obtained from solid-state reaction of cobalt carbonate and oxalic acid and decomposed at 400 ºC. As can be seen from this figure, the particles size is large and greater than 500 nm. The most particles haven't uniform shape. Fig. 2 shows the SEM image of cobalt oxide nanoparticles that obtained by second method. From the image, the diameters of the nanoparticles are around 60-100 nm. Each nanoparticle takes on a granular shape. It seems that the nanoparticles are size-homogeneous.

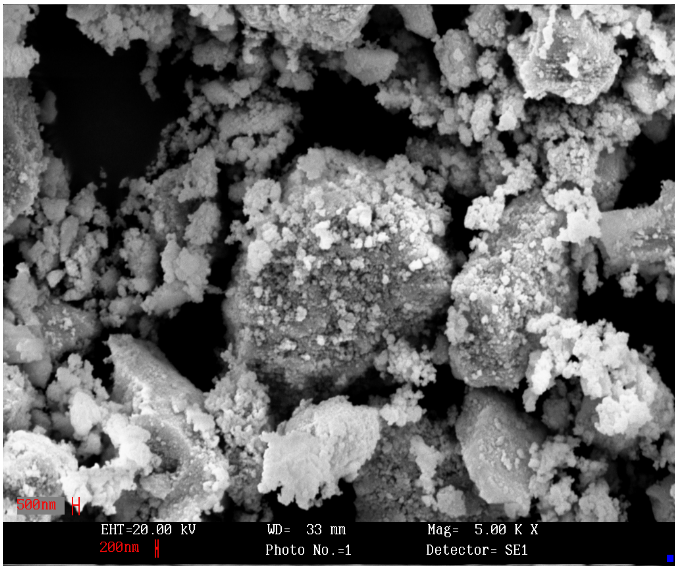

Fig. 1. SEM picture of cobalt oxide obtained from solid-state reaction of cobalt carbonate and oxalic acid in 70 ºC and then decomposed at 400 ºC

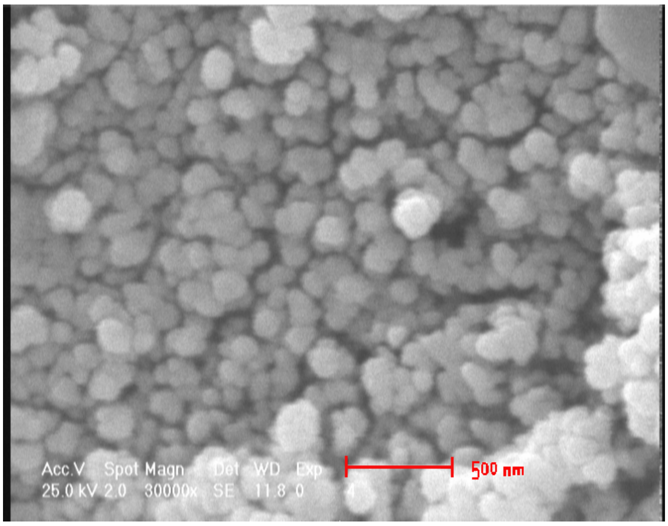

Fig. 2. SEM picture of cobalt oxide obtained from direct reaction of cobalt chloride and sodium hydroxide in 70 ºC and then decomposed at 400 ºC

Electrochemical properties of nanoparticles: Cobalt oxide nanoparticles used as electroactive substrate in carbon paste electrode (CPE). The cobalt oxides CPE, prepared from two methods were characterized by cyclic voltammetry. The CVs obtained for cobalt oxide CPE in 0.5 M phosphate buffer (pH 7) electrolyte, containing no deliberately added electroactive materials for second method nanoparticles are shown in Fig. 3a. The cobalt oxides CPE shows a single well-defined redox couple with formal potential, $E^{o\prime} = (E_{pa} + E_{pc})/2$, of 940 mV *vs.* SCE in phosphate buffer (pH = 7) as supporting electrolyte. The peak is not affected by stirring of electrolyte, offering proof that the material is well associated with the electrode surface under the solution conditions. The peak potential separations are 50 and 40 mV for first and second methods respectively with scan rate 20 mV s^{-1}. Cyclic voltammograms of the cobalt oxide CPE at different potential scan rates, between 0.7-1.1 V *vs.* SCE in 0.5 M phosphate buffer as supporting electrolyte were studied. The anodic and cathodic peak current of the voltammograms are linearly proportional to the square root of scan rate from 300 up to 800 mV s^{-1} and the ratio i_{pa}/i_{pc} remains almost equal to unity, as expected for a surface-type behaviour, which is expected for a diffusion controlled electrode process. Fig. 4 shows that variation of current as a function of scan rate for surface confine behaviour.

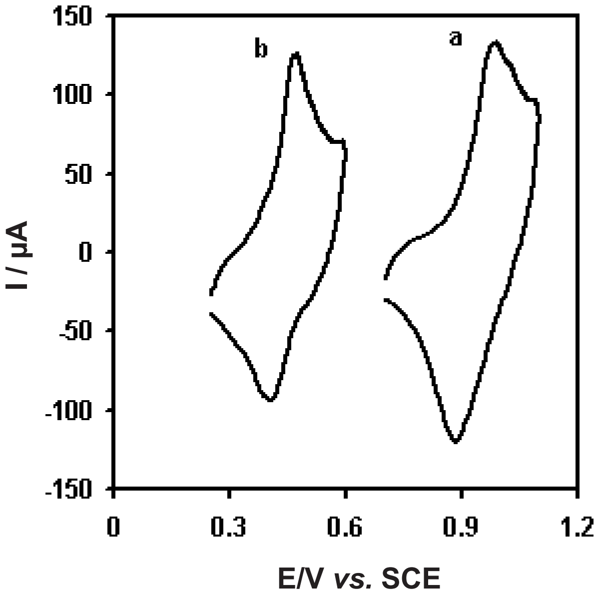

Fig. 3. Cyclic voltammograms for cobalt oxide nanoparticles obtained from second method in a) 0.5 M phosphate buffer (pH=7) b) 0.5 M NaOH as supporting electrolyte, scan rate 100 mV s^{-1}

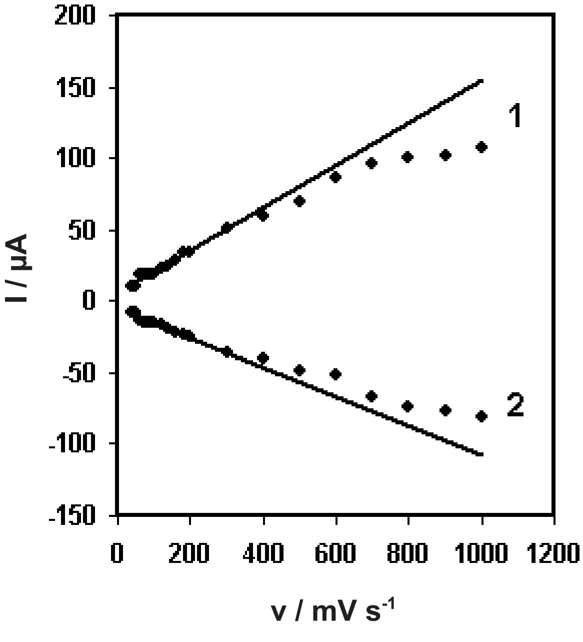

Fig. 4. Plot of anodic (1) and cathodic (2) peak currents *vs.* potential scan rate

The electrochemical behaviour of nanoparticles of cobalt oxides-CPE also studied in 0.5 M NaOH solution as supporting electrolyte, between 0.25-0.6 V *vs.* SCE. The obtained experimental results showed that in basic solutions the anodic and cathodic peak potentials shift about 0.510 V *vs.* SCE to less positive potential (Fig. 3b). In this case the formal potential was 0.430 V *vs.* SCE and the ratio i_{pa}/i_{pc} remains almost equal to unity. It seems the oxidation of Co(II) probably produces Co(III) in alkaline solution and oxidation of Co(III) to Co(IV) oxide species occurred during the positive scan in buffer as a supporting solution. According to the experimental results, scanning the cobalt oxide CPE, in basic solution between 0.25-0.6 V *vs.* SCE showed a pair of peak and only oxidation of Co(II) to Co(III) observed but in buffer solution scanning in this region shows the oxidation of Co(III) to Co(IV) oxide. It seems that buffer solution could stabilized the (III) and (IV) oxidation state of cobalt, which this couldn't occur in basic solution.

The electron transfer rate constant (k_s) and the transfer coefficient (α) can be determined by measuring the variations of peak potentials with a scan rate based on the method described by Laviron[22]. He has derived general expressions for the linear potential sweep voltammetric response for the case of surface-confined electroactive species. The values of peak separation (ΔE_P) were proportional to the logarithm of scan rate for scan rates of more than 0.8-7 V s^{-1}. The calculated values of (k_s) and (α) for cobalt oxide nanoparticles in CPE surface in buffer solution (pH = 7) were about 4.5 s^{-1} and 0.36, respectively.

The surface coverage Γ can be evaluated from the following equation:

$$\Gamma = Q/nFA$$

where Q is the charge obtained by integrating the anodic peak under the background correction (at a low scan rate of 20 mV s^{-1}) and the other symbols have their usual meanings. In the present case the calculated value of Γ is 4.5×10^{-9} mol cm^{-2}.

Effect of pH on the electrochemical properties nanoparticle CPE: Fig. 5 shows the pH-potential response curves for cobalt oxide nanoparticle CPE obtained from second method in 0.5 M phosphate buffer (pH 7) electrolyte. The experimental results shows that the nanoparticles obtained from second method response are better than the first in the pH ranges of 3-9. The slopes of curves were -62.7 mV/pH and 54.6 mV/pH for anodic and cathodic curve. The slopes of curve indicated that the pH response performance of these two kinds of nanoparticles was near-Nernstian. According to experimental results this electrode showed good response to pH and can be used as a solid-state pH sensor.

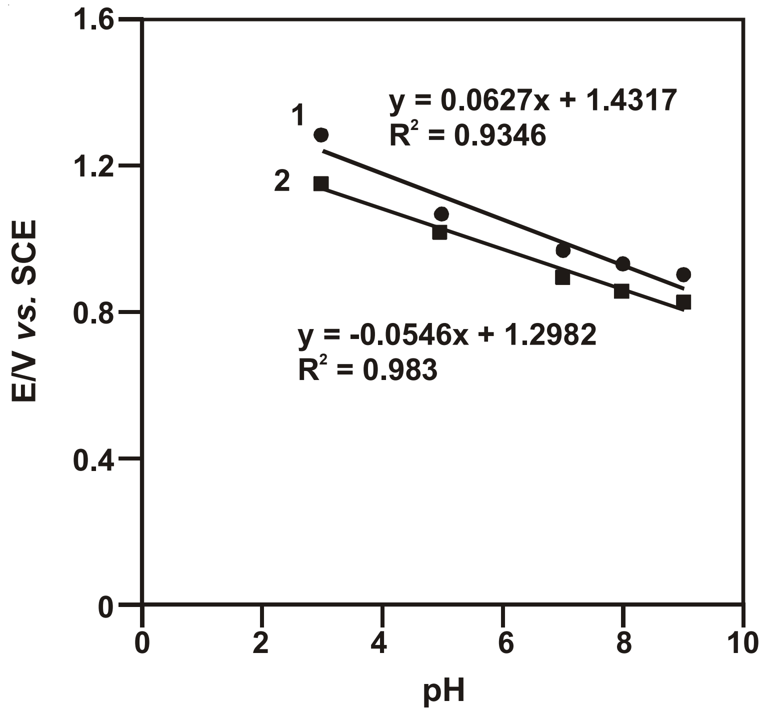

Fig. 5. Anodic peak (1) and cathodic peak (2) potential of cobalt oxide CPE *vs.* of pH for nanoparticles obtained from second method

Electrooxidation of fructose: The electrooxidation of fructose studied using cyclic voltammetry and chronoamperometric techniques. By succeeding adding different concentration of fructose to supporting electrolyte, an increase in the anodic peak current observed whereas the cathodic peak current is depressed. This behaviour is typical of that expected for mediated oxidation. The height of the anodic peak increases with increasing the fructose concentration and the plot of I_{pa} *vs.* fructose concentration between 0.4-25 mM is linear.

The chronoamperometric behaviour of fructose and cobalt oxide-CPE was examined in the absence and in the presence of fructose. For this purpose, 600 mV potential step was applied to the cobalt oxide-CPE immersed in 0.5 M NaOH containing various concentration of substrate. A typical chronoamperograms are presented in Fig. 6 As can be seen from this figure, by increasing fructose concentration, the current increased. This confirms the catalytic role of cobalt oxide-CPE in oxidation of fructose. From linear dependence of I to fructose concentration, it is concluded that the prepared CPE can be used as an amperometric sensor in fructose determination.

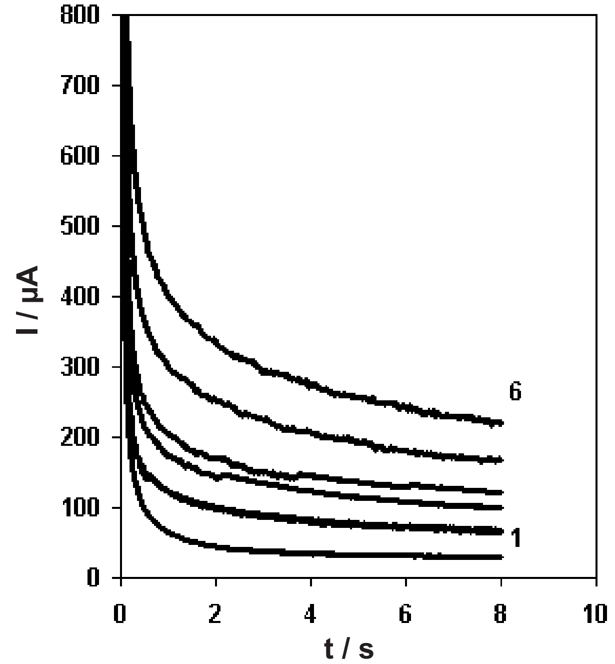

Fig. 6. Typical chronoamperograms obtained for cobalt oxide-CPE (1) in the absence and in the presence of (2) 3, (3) 6, (4) 9, (5) 14, (6) 22 mM fructose in the 0.5 M NaOH

Conclusion

Cobalt oxide powders have been synthesized using two different processes. After decomposing the nanoparticles at 400 ºC, CoO is produced. The obtained nanoparticles has been characterised by CV and SEM analysis. The effects of various experimental variables such as the cobalt chloride ratio, pH, applied potential, cycle number, *etc*. on the cobalt oxide CPE behaviour were evaluated.

The electrocatalytic activity of the cobalt oxide CPE in alkaline medium was explored by cyclic voltammeric techniques using fructose as model compounds of carbohydrates.

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