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Cobalt nanoflowers: Synthesis, characterization and derivatization to cobalt hexacyanoferrate—Electrocatalytic oxidation and determination of sulfite and nitrite

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ABSTRACT

Cobalt hexacyanoferrate (CoHCF) nanostructure was synthesized by anodic oxidation of metallic cobalt nanoflowers in a solution of $K_3Fe(CN)_6$. The synthesized CoHCF sample was then employed to prepare a modified carbon paste electrode. The modified electrode was characterized electrochemically in a phosphate buffer solution at physiological pH. Two redox transitions were appeared in the voltammograms which were related to the redox processes of Co^{II}/Co^{III} and Fe^{II}/Fe^{III} in the solid state of CoHCF. The modified electrode was successfully applied to the electrooxidation of nitrite and sulfite and these substrates were oxidized electrocatalytically on the modified electrode surface via the active Fe^{III} species. The catalytic rate constants, the electron transfer coefficients and diffusion coefficients involved in the electrocatalytic oxidation of the compounds were reported. The modified electrode was applied to the amperometric determination of nitrite and sulfite.

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1. Introduction

The recent advancement of nanoscience and nanotechnology has been accompanied by the synthesis of various sized and shaped nanostructured materials with novel characteristics [1]. In recent years, synthesis, characterization and applications of metal and metal oxide nanostructures have attracted the attention of researchers. In this regard, several synthesis methods have been employed for the preparation of nanoparticles, nanorods, nanowires, nanorings, nanotubes, nanosheets, nanoflakes and nanoflowers [2–8]. In comparison with bulk materials, size and shape of nanostructured materials affect their properties and potential applications [9–13].

Metal hexacyanoferrates (MHCFs) with a general formula of $M_a[Fe(CN)_6]_b \cdot nH_2O$ (M: a metal ion), as an important class of mixed-valence compounds, have a wide range of applications including sensors, optical control, ion exchanging, electrocatalysis and electrochromism [11,14]. Among the MHCFs, cobalt hexacyanoferrate (CoHCF) is very attractive for researchers, because of its unique chemical and electrochemical properties [11,14–16]. In CoHCF, both cobalt and iron have two oxidation states and redox couples of (II) and (III), leading to a multitude of compound stoichiometries, redox states and unique electrocatalytic and electrochromic properties, reversible photoinduced magnetization and thermochromism behavior in a wide range of temperatures [11,14–18].

Chemically modified electrodes have attracted much attention in the study of the kinetics of electrocatalytic oxidation and reduction of many important redox systems [19]. In such an electrode, an electrocatalytic system is generated and undergoes a rapid and reversible electrode reaction. On the other hand, modified electrodes can reduce the overpotential required for either oxidation or reduction of a substrate. Modified electrodes have a wide range of potential applications in electrochemical technology, energy conversion and storage systems, information storage, electrochromic, and display devices and in electroanalysis [10,15,16,20,21]. In this regard, immobilization of surface-active materials that can, in principle, alternate between various valence states under the effect of external electric fields is of particular interest. These surface-active materials are then capable of mediating fast electron transfer between a substrate in the bulk of the solution and the electrode surface. Among the chemically modified electrodes, carbon

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paste electrodes modified by MHCFs have been vastly studied [22].

In the present study, we report a novel and template-free approach to synthesize nanoflowers of cobalt. The nanoflowers were then derivatized to cobalt hexacyanoferrate and applied as a chemically modified electrode. The electrode represented fast faradaic reactions and showed a high efficiency toward the electrocatalytic oxidation of nitrite and sulfite as model compounds. Based on the results, an amperometric procedure was developed for the analysis of sulfite and nitrite with a high sensitivity and low detection limit.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade from Merck (otherwise those stated) and used without further purification. Carbon microparticles (graphite fine powder) with a particle size of less than 50 μm were also obtained from Merck. Polyvinylpyrrolidone (PVP, molecular weight 40,000) was purchased from Loba Chemie. All solutions were prepared with redistilled water.

2.2. Apparatus

Electrochemical measurements were carried out in a conventional three-electrode cell containing 100 mM Na-phosphate buffer solution, pH 7.4 (PBS) powered by an Autolab 302N potentiostat/galvanostat (The Netherlands). An Ag/AgCl, 3 M KCl and a platinum disk were used as the reference and counter electrodes, respectively. The system ran on a PC through GPES 4.9 software.

In order to obtain information about the morphology and size of the synthesized cobalt particles, scanning electron microscopy (SEM) was performed using a HITACHI Modele S-4160.

Powder X-ray diffraction (XRD) patterns were measured by a Philips X'Pert (The Netherlands) using CuKα radiation at 40 kV and 30 mA in the 2θ degree ranging from 35° to 80°.

2.3. Synthesis of cobalt nanoflowers

The cobalt nanoflowers were synthesized by the chemical reduction in the presence of PVP from a polyol medium the boiling point of the mixture. Hydrazine was employed as both reducing and complexing agents. PVP also acts as both complexing and structure-directing agents. In the synthesis procedure, 0.86 g $CoCl_2{\cdot}6H_2O$ and 4.0 g PVP were firstly dissolved in 180 mL ethylene glycol (EG) by intensive stirring. The stirring was continued for 12 h and after this time, a purple solution was obtained. Then, 20 mL hydrazine monohydrate (80% V/V) was added to the solution and continued to stirring for further 1 h. The solution color after this step was purple-pink. The mixture was subsequently heated to the boiling point of the resulting mixture (about 197 °C) by refluxing for 6 h. During this step, the solution color initially turned to dark, and finally, a dark precipitate was achieved. The system was then slowly cooled down on the heating mantel to room temperature. The final product was collected by centrifugation and washed with absolute ethanol for six times to remove all remnants. The product was dried under a nitrogen atmosphere and stored in degassed water. The final product was a loose dark powder.

2.4. Preparation of the working electrodes

Unmodified carbon paste electrode (UCPE) was prepared by hand-mixing carbon microparticles and mineral oil with an 80/20% (w/w) ratio. The paste was carefully mixed and homogenized in an agate mortar for 20 min. The resulting paste was kept at room temperature in a desiccator before use. The paste was packed firmly into a cavity (4.05 mm diameter, geometric surface are of 0.128 cm^2 and 0.5 mm depth) at the end of a Teflon tube. Electrical contact was established via a copper wire connected to the paste in the inner hole of the tube. The electrode surface was gently smoothed by rubbing on a piece of weighing paper just prior to use. This procedure was also used to regenerate the surface of the electrode.

Cobalt nanoflowers-modified carbon paste electrode (CoCPE) was prepared by hand-mixing carbon microparticles, mineral oil and cobalt nanoflowers with a 75/20/5% (w/w) ratio. Derivatization of cobalt nanoflowers to cobalt hexacyanoferrate and preparation of cobalt hexacyanoferrate-modified carbon paste electrode (MCPE) was performed by CoCPE anodizing. CoCPE was transferred to a 10 mL solution of 0.5 M KCl containing 0.5 M $K_3[Fe(CN)_6]$. Then, a positive potential of 1200 mV for 250 s was applied. During this step, the cobalt nanoflowers immobilized on the electrode surface, were oxidized under application of this highly positive potential to the cobalt ions. In the presence of hexacyanoferrate ions in the solution, these cobalt ions derivated to CoHCF and precipitated in situ on the nanoflowers surface.

3. Results and discussion

3.1. XRD

Fig. 1 represents an XRD pattern of cobalt nanoflowers. In the pattern, slightly broadened peaks appeared. It is due to the nanometer-size effect of the samples [23]. The crystal structure of the nanoflowers is hexagonal close-packed (hcp) structure. The main diffraction peaks at 42, 44.5, 48 and 76° are indexed to (1 0 0), (0 0 2), (1 0 1) and (1 1 0) reflections, respectively, of a hexagonal unit cell of a hcp cobalt structure (Joint Committee on Powder Diffraction Standards, JCPDS card No. 05-0727).

3.2. Electron microscopy

In order to investigate the surface morphology, structure and particle size, cobalt particles were examined by SEM. Fig. 2 shows SEM images of the synthesized cobalt particles with two different magnifications. It clearly reveals uniform flower-like microspheres with an average diameter of 5 μm. Higher magnification SEM indicates that the flowery microsphere is built of intercrossed 2D nanoflakes with a thickness of about 50 nm. All nanoflakes in a single flowery microsphere seem to grow from a center. They are aligned perpendicular to the surface of the spherical particles and the flakes are connected with each other via edge sharing to form nanoflakes unit. These results indicate that the flower-like cobalt nanostructure can be synthesized successfully by the simple reduction method from a polyol medium.

It has been reported that $CoCl_2$ forms a complex with PVP with a formula of $[(C_6H_9NO)_2CoCl_2]_x$, where x is the polymerization rate of PVP [24]. This complex is formed via oxygen atoms in carboxides and its nitrogen atoms in pyrrolidone rings due to the high polarity of the lactam ring conferred by resonance stabilization facilitated by near-planer ring geometry [25,26]. The resultant complex is soluble in organic alcohols [26]. Therefore, the complex of PVP-$CoCl_2$ in such a reaction system is formed. In consequence, a more stable $Co[(N_2H_4)_3]^{2+}$ complex is formed. The reactions are as follows:

$$CoCl_2 + PVP \rightarrow CoCl_2\text{–}PVP(complex) \quad (1)$$

$$CoCl_2\text{–}PVP + 3N_2H_4 \rightarrow Co[(N_2H_4)_3]^{2+} + PVP + 2Cl^- \quad (2)$$

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