Morphology-controlled synthesis of cobalt nanostructures by facile electrodeposition: transition from hexagonal nanoplatelets to nanoflakes

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ABSTRACT

Cobalt hexagonal nanoplatelets and cobalt nanoflakes were produced by electrodeposition onto aluminium from cobalt sulphate solutions. The dependence of the nanostructure morphology on cobalt ion concentration and potential was investigated under potentiostatic and pulsed-electrodeposition. Under potentiostatic electrodeposition, cobalt hexagonal nanoplatelets were obtained with cobalt ion concentration equal to 0.01 and 0.1 M, while cobalt hydroxide nanoflakes were formed as the cobalt ion concentration was increased to 0.2 M. Under pulsed electrodeposition, both hexagonal nanoplatelets and hydroxide nanoflakes could be obtained with cobalt ion concentration equal to 0.1 M by modulation of the imposed current/potential wave. The analysis of the current transients recorded under potentiostatic electrodeposition and the microscopic analysis of the deposits indicate that three-dimensional diffusion control cannot adequately describe the growth of the cobalt nanostructures. We propose that an aggregative growth mechanism involving the formation and the surface diffusion of cobalt nanoclusters can explain the influence of electrodeposition parameters on the morphology of the cobalt nanostructures.

1. Introduction

The application of cobalt nanostructured materials has attracted interest in numerous technological areas including, for example, the production of chemical sensors [1], high-performance cathodes for alkaline-hybrid batteries [2], and catalysts for water splitting [3] and hydrogen evolution reactions [4]. In any application, the achieved performances are largely influenced by the morphology of the cobalt nanostructures. Nanostructure morphology can, for example, affect the electrochemical efficiency of supercapacitors [5] and dictate the mechanism and the rate of electro-catalysed reactions [6].

During the past years, numerous synthesis routes were developed which allowed producing cobalt nanostructures with different morphologies. Examples of synthesized cobalt nanostructures include nanowires [7], nanotubes [8], nanodiscs [9], nanosheets [10] and nanoplatelets [11].

If large throughputs are required, solution phase methods represent the most appropriate route to synthesize cobalt nanostructures. If solution phase methods are implemented, template agents as, for example, surfactants can be adopted to control the morphology of synthesized nanostructures. Examples of application of such an approach are the synthesis of hexagonal disk-shaped cobalt nanocrystals by cobalt carbonyl decomposition in presence of linear amines [12] and the production of cobalt nanoflakes by chemical precipitation [13]. The surfactant-free synthesis of cobalt hydroxide nano-flowers at room temperature was reported by Modal et al. [14].

Electrodeposition becomes particularly attractive when the immobilization of nanostructures onto conductive substrates is required. Compared to solution phase methods, electrodeposition can enhance the controllability of nanostructure morphology [15]. Morphologies spanning from compact faceted nanocrystals to dendritic and fractal nanostructures can be generated by varying the electrode potential and/or the concentration of the precursor metal ion. Spherical, worm and grain like cobalt oxide nanoparticles were electrodeposited onto glassy carbon electrode by cyclic voltammetry [16] while a network of nano-layered cobalt hydroxide sheets was obtained by potentiostatic electrodeposition from cobalt nitrate solution [11]. Cobalt nanostructures with tree-like morphology were synthesized by potentiostatic electrodeposition onto a self-assembled gold nanoparticle modified glassy

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carbon electrode [17]. Isolated aggregates of cobalt nanoparticles were generated by pulsed current electrodeposition [18].

Recently, attention has been devoted to the electrochemical synthesis of cobalt hydroxide nanoflakes [19,20]. These are nanoporous structures composed of interconnected sheets with thickness and crystallite size around 10 nm [21,22]. Such characteristics, which ensure sustained catalytic and electrochemical activity, can be exploited to develop hierarchically structured porous materials [23]. For example, hierarchically porous pseudo-capacitors were produced by electrodeposition of cobalt nano-flakes onto nickel foam [21].

The method commonly implemented to synthesize cobalt hydroxide nanoflakes is the electrochemical reduction of nitrates in presence of a cobalt salt [24]. Nitrate reduction is performed at potential greater than the equilibrium potential of cobalt ion reduction, which prevents cobalt electrodeposition. The generation of OH^- by nitrate reduction increases the pH at the electrode surface and induces the precipitation of cobalt hydroxide. Cobalt hydroxide nanoflakes synthesized by the nitrate reduction method were, for example, tested as supercapacitors in alkaline-hybrid batteries [25] and oxygen evolution anodes in the water splitting process [23].

Alternatively, cobalt nanoflakes can be synthesized by electrochemical reduction of cobalt ions at potential values that allow for the co-reduction of water and protons [26]. If this method is implemented, cobalt nanoparticles are formed during the early stage of electrodeposition, which causes the depletion of cobalt ions near the electrode. Water reduction then takes place catalysed by electrodeposited cobalt nanoparticles. This increases the pH near the electrode and can induce cobalt hydroxide precipitation. The occurrence of supersaturation near the electrode and the consequent cobalt hydroxide precipitation are determined by the interplay between the consumption of cobalt ions, by electrochemical nucleation and growth of cobalt nanoparticles, and the generation of OH^- by reduction of water and protons. If the consumption of cobalt ions by electrochemical nucleation and growth is much faster than the generation of OH^-, the solubility product of cobalt hydroxide cannot be achieved and precipitation is prevented. On the other hand, cobalt hydroxide precipitation can be induced by modifying the electrodeposition parameters (potential, concentration of cobalt ions) in a way that decreases the consumption rate of cobalt by electrochemical nucleation and growth and increases the reduction rates of water and protons.

In accordance with the analysis illustrated above, the electro-chemical reduction method may be implemented to produce cobalt films with different morphologies and structures. Transition from deposits composed of only cobalt nanoparticles to structured films composed of cobalt nanoparticles and cobalt hydroxide nanoflakes can be generated by controlling the ratio between the consumption rate of cobalt and the generation rate of OH^-. Structured films composed of metallic cobalt nanoparticles and cobalt hydroxide nanoflakes can offer several advantages compared to films composed of only cobalt hydroxide nanoflakes. In the production of supercapacitors for alkaline hybrid batteries, for example, increasing the fraction of metallic cobalt nanoparticles can enhance the electric conductivity and the mechanical properties of the film [26].

Nevertheless, little efforts have been devoted to exploiting the versatility of the electrochemical reduction method. Very few studies reported the production of cobalt nanoflakes by electro-chemical reduction of cobalt ions [26], while no study investigated the interaction between the formation of cobalt nanoparticles and the generation of OH^- that govern transition between different morphologies.

In the application of the electrochemical reduction method, central role is played by the characterization of the mechanisms that drive electrochemical nucleation and growth of cobalt nanoparticles. These mechanisms ultimately determine the profiles of cobalt ion concentration and pH in the electrolyte and can thus dictate the boundaries of the parameter space marking transition between metallic nanoparticles and hydroxide nanoflakes. Previous studies have reported that the electrodeposi-tion of cobalt nanoparticles is governed, irrespective of the nucleation rate, by three-dimensional diffusion control [27–29]. This conclusion has been frequently justified by the satisfactory fitting between potentiostatic current transients and the predic-tions of the Scharifker and Mostany model (SM) model [28,29], which indeed describes multiple nucleation and growth under three-dimensional diffusion control. Notably, most of the above-mentioned studies have not analysed the reliability of the nucleation parameters estimated by fitting the SM model to potentiostatic current transients. This can be done, for example, by comparing the number densities estimated by fitting with those determined by microscopic analysis of the deposits. Remarkably, in only one study and for only one set of parameters we could find such an analysis [30], while the characterization of the nucleation and growth mechanisms was limited in any other study to the fitting of the SM model to current transients.

In this article, we demonstrate that the electrochemical reduction of cobalt ions can be implemented to produce cobalt nanoplatelets with controlled size and structured films composed of cobalt nanoparticles covered by cobalt hydroxide nanoflakes. The analysis is focused on elucidating the mechanisms that govern transition between cobalt nanoparticles and cobalt hydroxide nanoflakes. For this purpose, the influence of electrode potential and cobalt ion concentration on the morphology of synthesized nanostructures is investigated under potentiostatic operation. The mechanisms of cobalt nucleation and growth are characterized by combined electrochemical analysis of the potentiostatic current transients and microscopic analysis (scanning field electron microscopy (SEM), atomic force microscopy (AFM)) of the electrodeposited nanostructures. Chemical characterization of the electrodeposited nanostructures is performed by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). A pulsed electrodeposition strategy is implemented that allows controlling transition from cobalt nanoplatelets to structured nano-porous films at any prescribed concentration and potential.

2. Materials and methods

2.1. Solutions

Reagent grade (Sigma-Aldrich *ReagentPlus®*) $CoSO_4 \cdot 7H_2O$, Na_2SO_4 and H_3BO_3 were used to prepare solutions with Co^{2+} concentration equal to 0.01 M, 0.1 M and 0.2 M. Na_2SO_4 and H_3BO_3 concentrations equal to 1 M and 0.5 M, respectively, were used in any solution. H_3BO_3 was used to buffer the pH increase induced by the co-reduction of water and protons. The pH of any solution was found to be around 4.7.

2.2. Electrochemical setup

A three electrode jacketed glass cell without agitation was employed to perform any electrodeposition test. A spiral Pt wire and aluminium foil with surface equal to 0.5 cm^2 (Alfa Aesar 99%, 0.25 mm thickness) were the counter and the working electrode, respectively. An Ag/AgCl saturated electrode was used as reference electrode. Potential values reported throughout the manuscript are