



# Two-step one-pot electrosynthesis and catalytic activity of $x\text{CoO}-y\text{Co}(\text{OH})_2$ -supported silver nanoparticles

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Received: 14 January 2020 / Revised: 17 February 2020 / Accepted: 18 February 2020 / Published online: 2 March 2020  
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## Abstract

Efficient two-step electrosynthesis of  $x\text{CoO}-y\text{Co}(\text{OH})_2$  ( $\text{CoO}_x\text{H}_y$ )-supported silver nanoparticles (AgNPs) is carried out in *N,N*-dimethylformamide (DMF) using atmospheric oxygen as a reagent and mediator at the potentials of its reduction to the superoxide ion. In the first step, the reduction of oxygen in the presence of Co (II) ions added to the solution as a salt or generated upon dissolution of a Co anode by means of electrolysis results in a mixture of amorphous cobalt oxide CoO and its hydrated form Co(OH)<sub>2</sub>. The addition of Ag<sup>+</sup> ions to the resulting solution of  $\text{CoO}_x\text{H}_y$  by similar methods results in two parallel reactions of Ag<sup>+</sup> reduction to give AgNPs: reversible reduction by CoO and irreversible reduction by DMF. In the second step, oxygen-mediated electroreduction of  $\text{CoO}^+$  and residual quantities of Ag<sup>+</sup> occurs, as well as regeneration of  $\text{CoO}_x\text{H}_y$ . The resulting spherical AgNPs are bound and stabilized by the  $\text{CoO}_x\text{H}_y$  matrix. Both steps occur quantitatively and consume the theoretical amount of electricity (2 F with respect to  $\text{Co}^{2+}$  in the first step and 1 F with respect to Ag<sup>+</sup> in the second step). Depending on the production method, the size of the AgNPs varies in a range from  $7\pm 2$  to  $27\pm 10$  nm. The Ag/ $\text{CoO}_x\text{H}_y$  nanocomposites obtained exhibit catalytic activity in the *p*-nitrophenol reduction with sodium borohydride in an aqueous medium. Their activity caused by AgNPs significantly increases in the presence of cetyltrimethylammonium chloride (CTAC), a micelle-forming cationic surfactant.

**Keywords** electrochemical synthesis · oxygen-mediated electroreduction · silver · cobalt(II) oxide · nanocomposite

## Introduction

The keen interest in metal nanoparticles (MNPs) is due to the unique physical and chemical properties of these particles and the wide variety of their potential use in catalytic, biomedical, optical, electronic, sensing, and other applications [1–7]. In terms of catalysis, MNPs immobilized on dispersed or soluble stable nanoparticles of various natures are of considerable

interest. In particular, polymers [8, 9], porous carbon [10, 11], modified carbon nanotubes [12, 13], oxidized graphene [14, 15], silica NPs ( $\text{SiO}_2$ ) [16–18], and metal oxides [19–22] can be used as supports for MNPs. The major part of the MNP surface in such nanocomposites remains free and retains catalytic activity, while the immobility of MNPs provides their stability against aggregation. If the distribution of nanocomposites in solution is homogeneous, the entire volume is the catalytic reaction zone. Therefore, diffusion limitations typical of heterogeneous reactions are lifted. Moreover, MNPs act as heterogeneous catalysts, and the term “pseudo-homogeneous catalysts” is applicable to them.

Among pseudo-homogeneous catalysts, MNPs immobilized on metal oxides ( $\text{M}^1/\text{M}^2\text{O}_x$ ) are of particular interest. Metal oxides catalyze a variety of reactions (oxidation, reduction, coupling to give C–C and C–O bonds, condensation, and others) [23–30], and in combination with MNPs they can serve not only as supports or stabilizers of MNPs but also as active co-catalysts, providing bifunctionality or a synergistic effect to a composite. The facility of catalyst separation after a catalytic reaction is yet another advantage of MNP

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10008-020-04526-0>) contains supplementary material, which is available to authorized users.

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