

## CoO–*x*Co(OH)<sub>2</sub> supported silver nanoparticles: electro-synthesis in acetonitrile and catalytic activity

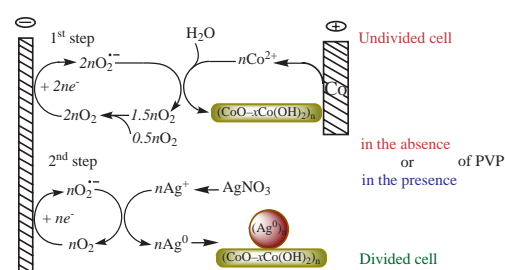
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**The two-step electro-synthesis of the nanocomposites of silver nanoparticles supported on CoO–*x*Co(OH)<sub>2</sub> was carried out in acetonitrile using dissolved oxygen as a reagent in the first step (support synthesis) and a mediator in the second step (silver nanoparticle synthesis). The support and nanocomposite catalyzed the reduction of *p*-nitrophenol with sodium borohydride in an aqueous medium, and poly(*N*-vinylpyrrolidone) decreased their catalytic activity.**



**Keywords:** electrochemical synthesis, oxygen-mediated electroreduction, silver, cobalt(II) oxide, nanocomposite, catalysis.

Immobilized metal nanoparticles (MNPs) are of interest as highly efficient pseudohomogenic metal nanocatalysts.<sup>1,2</sup> Different materials, such as polymers,<sup>3</sup> porous carbon,<sup>4</sup> modified carbon nanotubes,<sup>5</sup> oxidized graphene,<sup>6</sup> fullerenes,<sup>7</sup> silica NPs,<sup>8,9</sup> and metal oxides,<sup>9–11</sup> can be used as supports. Metal oxides catalyze various reactions;<sup>12</sup> in combination with MNPs, they can function not only as a support but also as an active cocatalyst. The composites of MNPs with metal oxides can be produced by chemical<sup>9,10</sup> or electrochemical<sup>11</sup> synthesis.

Recently,<sup>13,14</sup> we proposed a two-step electro-synthesis of similar nanocomposites using dissolved oxygen as a reagent and mediator. At the first step, the superoxide ion generated by oxygen reduction reacts with a metal ion M<sup>I</sup> to form a metal oxide M<sup>I</sup>O<sub>*x*</sub>, and it reduces metal ions M<sup>II</sup> to M<sup>II</sup>NPs at the second step. The process was tested by synthesizing M<sup>II</sup>/[CoO–*x*Co(OH)<sub>2</sub>] (M<sup>II</sup> = Ag, Au, Pd) nanocomposites in DMF. In this case, the irreversible chemical reduction of M<sup>II</sup> ions with DMF catalyzed by cobalt hydroxide was superimposed with mediated electrochemical reduction of M<sup>II</sup> ions.

In this work, we performed a similar two-step electro-synthesis of an Ag/CoO–Co(OH)<sub>2</sub> nanocomposite in an acetonitrile solvent in the absence and in the presence poly(*N*-vinylpyrrolidone) (PVP) as a stabilizer of MNPs at room temperature.

A cyclic voltammetry (CV) study was performed to select the conditions of electrolysis. The CV curve of O<sub>2</sub> in the acetonitrile/0.1 M Bu<sub>4</sub>NBF<sub>4</sub> system exhibited two reduction peaks<sup>†</sup> due to the reversible reduction of O<sub>2</sub> to the O<sub>2</sub><sup>•–</sup> superoxide ion and the irreversible reduction of O<sub>2</sub><sup>•–</sup>, respectively.<sup>15,16</sup> The concentration of O<sub>2</sub> in solution was ~3.3 mM, as follows from a comparison between the currents of the first peaks of O<sub>2</sub> and the one-electron reduction of methyl viologen. PVP had no effect on the reduction of O<sub>2</sub> and the stability of the superoxide ion.<sup>†</sup> Co<sup>2+</sup> was reduced in two steps to form metallic cobalt, which was

deposited on the electrode and easily oxidized at A<sup>Co</sup> peak potentials.<sup>†</sup> The CV curve of the (O<sub>2</sub> + 3.0 mM Co<sup>2+</sup>)<sup>†</sup> two-component system differed significantly from the additive curve of the individual components: (i) a low-expressed prepeak appeared at E<sub>p</sub> = –0.78 V; (ii) the first O<sub>2</sub> reduction peak current corresponded to the total reduction current of O<sub>2</sub> and Co<sup>II</sup>; (iii) the oxidation current of superoxide ions decreased; and (iv) the second reduction peak of Co<sup>II</sup> and the oxidation peak of A<sup>Co</sup> disappeared. The resulting CV data indicate the rapid consumption of a part of generated superoxide ions due to the quantitative binding of Co<sup>II</sup> ions to form CoO–*x*Co(OH)<sub>2</sub>. In the presence of PVP, the process proceeded similarly [Figure S1(b)].

The preparative electro-synthesis of the CoO–*x*Co(OH)<sub>2</sub> support was carried out at controlled potentials of O<sub>2</sub> reduction to the superoxide ion (E = –1.10 V vs. SCE) in an undivided cell with the generation of Co<sup>2+</sup> ions by electrolysis with a Co anode in the absence (experiment 1) and in the presence (experiment 2) of 20 mM PVP. The electrolysis proceeded smoothly without electrode passivation in all cases. The Co anode was dissolved with a current efficiency of about 120%. Color, CV, data from DLS method, UV-VIS spectra of the resulting solutions and IR spectra of the isolated solid precipitates<sup>†</sup> were as previously described for CoO–*x*Co(OH)<sub>2</sub> (Table 1).<sup>13,14</sup>

The presence of oxygen and cobalt in NPs was also confirmed by elemental microanalysis.<sup>†</sup> According to DLS data, PVP in solution stabilizes the support NPs of a specific size (18 nm), while polydisperse particles were obtained in the absence of a stabilizer. The particles stick together, lose identity, and form a single common matrix<sup>†</sup> [Figures 1(a), 1(c)] on the solid substrate. According to XRD data, the CoO–*x*Co(OH)<sub>2</sub> and CoO–*x*Co(OH)<sub>2</sub>/PVP particles possessed amorphous structure.<sup>†</sup>

<sup>†</sup> See Online Supplementary Materials for details.