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CoO–xCo(OH)$_2$ supported silver nanoparticles: electrosynthesis in acetonitrile and catalytic activity

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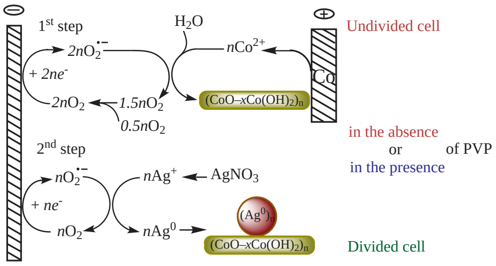
The two-step electrosynthesis of the nanocomposites of silver nanoparticles supported on CoO–xCoO(OH)$_2$ was carried out in acetonitrile using dissolved oxygen as a reagent in the first step (support synthesis) and a mediator in the second step (silver nanoparticle synthesis). The support and nanocomposite 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.[1,2] Different materials, such as polymers,[3] porous carbon,[4] modified carbon nanotubes,[5] oxidized graphene,[6] fullerenes,[7] silica NPs,[8,9] and metal oxides,[9–11] can be used as supports. Metal oxides catalyze various reactions;[12] 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[9,10] or electrochemical[11] synthesis.

Recently,[13,14] we proposed a two-step electrosynthesis 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^1 to form a metal oxide M^1O_x, and it reduces metal ions M^2 to M^2NPs at the second step. The process was tested by synthesizing M^2/[CoO–xCo(OH)$_2$] (M^2 = Ag, Au, Pd) nanocomposites in DMF. In this case, the irreversible chemical reduction of M^2 ions with DMF catalyzed by cobalt hydroxide was superimposed with mediated electrochemical reduction of M^2 ions.

In this work, we performed a similar two-step electrosynthesis of an Ag/CoO–Co(OH)$_2$ 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_2 in the acetonitrile/0.1 M Bu_4NBF_4 system exhibited two reduction peaks[†] due to the reversible reduction of O_2 to the $O_2^{\bullet -}$ superoxide ion and the irreversible reduction of $O_2^{\bullet -}$, respectively.[15,16] The concentration of O_2 in solution was ~3.3 mM, as follows from a comparison between the currents of the first peaks of O_2 and the one-electron reduction of methyl viologen. PVP had no effect on the reduction of O_2 and the stability of the superoxide ion.[†] Co^{2+} was reduced in two steps to form metallic cobalt, which was deposited on the electrode and easily oxidized at A^{Co} peak potentials.[†] The CV curve of the (O_2 + 3.0 mM Co^{2+})[†] two-component system differed significantly from the additive curve of the individual components: (i) a low-expressed prepeak appeared at E_p = –0.78 V; (ii) the first O_2 reduction peak current corresponded to the total reduction current of O_2 and Co^{II}; (iii) the oxidation current of superoxide ions decreased; and (iv) the second reduction peak of Co^{II} and the oxidation peak of A^{Co} disappeared. The resulting CV data indicate the rapid consumption of a part of generated superoxide ions due to the quantitative binding of Co^{II} ions to form CoO–xCo(OH)$_2$. In the presence of PVP, the process proceeded similarly [Figure S1(*b*)].

The preparative electrosynthesis of the CoO–xCo(OH)$_2$ support was carried out at controlled potentials of O_2 reduction to the superoxide ion (E = –1.10 V *vs.* SCE) in an undivided cell with the generation of Co^{2+} 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[†] were as previously described for CoO–xCo(OH)$_2$ (Table 1).[13,14]

The presence of oxygen and cobalt in NPs was also confirmed by elemental microanalysis.[†] 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[†] [Figures 1(*a*), 1(*c*)] on the solid substrate. According to XRD data, the CoO–xCo(OH)$_2$ and CoO–xCo(OH)$_2$/PVP particles possessed amorphous structure.[†]

[†] See Online Supplementary Materials for details.

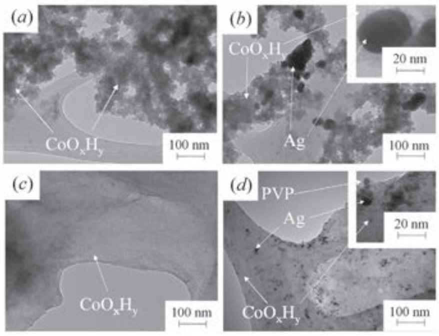
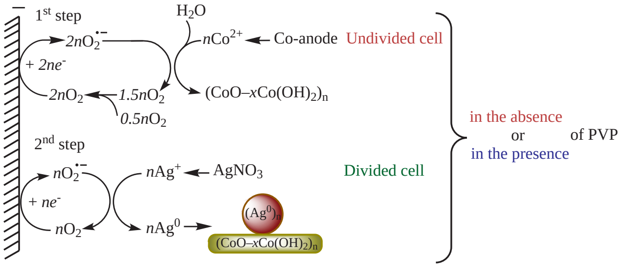


Figure 1 TEM images of CoO–xCo(OH)$_2$ and CoO–xCo(OH)$_2$/PVP supports and Ag/CoO–xCo(OH)$_2$ and Ag/CoO–xCo(OH)$_2$/PVP nanocomposites obtained in experiment nos. (*a*) 1, (*b*) 1-2, (*c*) 2, and (*d*) 2-2.

Thus, amorphous CoO–xCo(OH)$_2$ was formed in the electrolysis at the potentials of oxygen reduction to the superoxide ion in acetonitrile and in DMF (Scheme1).

After the addition of 1.5 mM AgNO$_3$ to the solutions of CoO–xCo(OH)$_2$ and CoO–xCo(OH)$_2$/PVP (experiments 1-1 and 2-1), the solution color did not change for 1 h.† In the absence of PVP, the height of the Ag$^+$ reduction peak remained unchanged.† In the presence of PVP, the C_1^{Ag} peak decreased and an additional C_2^{Ag} peak appeared. Two oxidation peaks of deposited metallic silver (A_1^{Ag} and A_2^{Ag}) were observed in the anodic CV region.† The sum of the C_1^{Ag} and C_2^{Ag} peak currents corresponds to the concentration of silver ions in the solution. PVP does not affect the CV of individual Ag ions.† In the 3 mM Co(BF$_4$)$_2$–1.5 mM AgNO$_3$–20 mM PVP system, the Ag$^+$ reduction peak remained at Bu$_4$NOH concentrations of 0.40 and 0.72 mM, but the peak was split into two peaks when the concentration increases to 1.5 mM, as in the above experiment.† Apparently, AgOH was obtained after the addition of Ag$^+$ ions to a solution of CoO–xCo(OH)$_2$/PVP.



Scheme 1 Electrosynthesis of CoO–xCo(OH)$_2$-supported silver nanoparticles (AgNPs) in acetonitrile.

According to CV data, the chemical reduction of Ag$^+$ ions does not occur in the solutions of CoO–xCo(OH)$_2$ and CoO–xCo(OH)$_2$/PVP. This was confirmed by the UV-VIS spectra and XRD patterns.†

The second step of the synthesis was carried out in the cathodic space of a divided cell at the potential E = –1.10 V passing an amount of electricity theoretically necessary to reduce 1.5 mM of Ag$^+$ ions (1 F) (experiments 1-2 and 2-2†). After that, the Ag$^+$ and AgOH reduction peaks disappeared completely and only O$_2$ reduction peaks were present in the cathode potential region of the CV.† Thus, the Ag$^+$ ions were quantitatively reduced after passing a theoretical amount of electricity due to a high efficiency of oxygen-mediated reduction of Ag$^+$ ions (Scheme 1).

Absorption bands due to CoO–xCo(OH)$_2$ and AgNPs were presented in the UV-VIS spectra† of the resulting solutions.[2] According to DLS, PVP stabilized individual composite nanoparticles (28 nm), which aggregated to form larger particles (1280 nm)† in the absence of PVP. According to the SEM and TEM images [Figures 1(*b*) and 1(*d*)] and the energy dispersive spectra, individual spherical AgNPs immobilized on CoO–xCo(OH)$_2$ were formed in both experiments.† The particle size in the absence of PVP (35 ± 15 nm) was substantially higher than

Table 1 Synthesis conditions, characteristics and catalytic activity of CoO–xCo(OH)$_2$, CoO–xCo(OH)$_2$/PVP, Ag/CoO–xCo(OH)$_2$ and Ag/CoO–xCo(OH)$_2$/PVP nanocomposites obtained by electrolysis at the controlled potential of oxygen reduction in acetonitrile/0.1 M Bu$_4$NBF$_4$. C_{Ag+} = 1.5 mM, C_{CoO} = 3.0 mM, 295 K.

Experiment no.	NP	Q^a/F	NP size/nm				λ^g/nm	Catalytic activity of NP in *p*-nitrophenol reduction^h		Reference
			DLS		Electron microscopy					
			D_h^b	PDI^c	SEM^{d,e}	TEM^{d,f}		k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}	
1	CoO–xCo(OH)$_2$	2	1–220 96^d, 208^d	0.977			291, 428 285^d, 409^d	6.5×10^{-4}		This work
1-1	CoO–xCo(OH)$_2$ + 1.5 mM AgNO$_3$	2	342–1106	0.825			294, 425			This work
1-2	Ag/CoO–xCo(OH)$_2$	3	1281 38^d	0.228	53±14	25±9	294, 398 287^d, 390^d	3.3×10^{-3}	1.7×10^3	This work
2	CoO–xCo(OH)$_2$/PVP	2	18 28^d	0.226			266, 387 261^d, 381^d	2.8×10^{-4}		This work
2-1	CoO–xCo(OH)$_2$/PVP + 1.5 mM AgNO$_3$	2	21	0.239			265, 398			This work
2-2	Ag/CoO–xCo(OH)$_2$/PVP	3	28 58^d	0.197	11±4	6±2	272, 393 259^d, 412^d	6.6×10^{-4}	3.3×10^2	This work
	CoO–xCo(OH)$_2$	2	50–1283 94^d	0.413			285, 357 285^d, 380^d	3.1×10^{-6}		13
	Ag/CoO–xCo(OH)$_2$	3	872 62^d	0.501	22±9	7±2	280, 444 265^d, 424^d	4.2×10^{-4}	2.1×10^2	13
	CoO–xCo(OH)$_2$/PVP	2	8–21 91^d					9.1×10^{-6}		14
	Ag/CoO–xCo(OH)$_2$/PVP	3	21 91^d		8±3	5±2	426 442^d	2.0×10^{-4}	1.0×10^2	14

[a] The amount of electricity with respect to Co^{2+}; [b] the average hydrodynamic diameter of particles; [c] polydispersity index; [d] NP isolated and dispersed in ethanol; [e] the size of AgNPs with stabilizer shell; [f] AgNPs size; [g] wavelength of NP absorption band in UV-VIS spectrum; [h] $C_{(p\text{-nitrophenol})}$ = 0.1 mM, $C_{(NaBH_4)}$ = 5 mM, $C_{(MNP)} = 2 \times 10^{-6}$ M, $C_{(CoO–xCo(OH)_2)} = 4 \times 10^{-6}$ M (experiments 1, 1-2, 2 and 2-2); $C_{(PVP)} = 2.6 \times 10^{-5}$ M, H$_2$O.

that in the presence of PVP (6 ± 2 nm). According to XRD data,† the sizes of metallic silver crystallites were also higher [32.89 (71)–51.7(11) and 2.90(7)–4.6(1) nm, respectively]. It is obvious that PVP binds and stabilizes not only the support and nanocomposite but also the AgNPs. Apparently, the AgNPs stabilized by PVP are bound on the CoO–xCo(OH)$_2$ support.

The catalytic activity of the supports and nanocomposites was tested in the reduction reaction of *p*-nitrophenol with a 50-fold excess of sodium borohydride in water. This reaction is catalyzed by metal nanoparticles[16,17] and metal oxides (TiO_2, Cu_2O, and Fe_2O_3).[18] With the addition of the nanocomposites (2 mol% Ag with respect to *p*-nitrophenol), a decrease in the absorption band of *p*-nitrophenolate at 400 nm and an increase in the *p*-aminophenol (reduction product) absorption band at 300 nm were observed.† The supports and nanocomposites were catalytically active in this reaction, however their activity became noticeable only after an induction period of 4–13 min.† The pseudo-first-order rate constants[17(g)] (k_1) and the catalytic activity of the nanocomposites (k_2) calculated as a ratio of k_1 to the molar concentration of AgNPs are summarized in Table 1. The nanocomposites exhibited greater activity than that of the support, and PVP markedly decreased the activity of both the support and the composite because a PVP shell may limit the access of reagents to the surface. The CoO–xCo(OH)$_2$ support produced in DMF did not show catalytic activity either individually or in a nanocomposite with AgNPs in the reduction of *p*-nitrophenol carried out under identical conditions in an aqueous solution (see Table 1).[13,14] From this viewpoint, the catalytic and co-catalytic activity of the nanosupport obtained in acetonitrile is unexpected. The reason for different catalytic activities of the supports prepared in different solvents is unclear. The solvents can be involved in the catalytic reaction because they are added, although in small amounts, to the reaction medium together with the catalyst.

Thus, we carried out the two-step electrosynthesis of AgNPs on a pure CoO–xCo(OH)$_2$ support in acetonitrile using atmospheric oxygen as a reagent and mediator at the potentials of its reduction to the superoxide ion. Both steps proceed with high efficiency. The catalytic activity of these nanoparticles of supports and composites in the reduction reaction *p*-nitrophenol with sodium borohydride in an aqueous medium was higher as compared to those obtained in DMF.

The IR spectral and X-ray diffraction analyses were carried out using the equipment of the Assigned Spectral-Analytical Center at the Kazan Scientific Center, Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.07.016.

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