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Formation of ternary nanostructures NiCo-Pd by galvanic replacement of Pd^{2+} on bimetallic NiCo nanoparticles

Liliya BAZYLYAK[1,2]*, Yaroslav PILYUK[1], Ihor HALATYN[1], Pavlo LYUTYY[3], Andriy KYTSYA[1,2]

[1] *Department of Physical Chemistry of Fossil Fuels, Institute of Physical Organic Chemistry and Coal Chemistry named after L.M. Lytvynenko of the National Academy of Sciences of Ukraine, Naukova St. 3a, 79060 Lviv, Ukraine*
[2] *Karpenko Physico-Mechanical Institute of the National Academy of Sciences of Ukraine, Naukova St. 5, 79060 Lviv, Ukraine*
[3] *Lviv Polytechnic National University, Bandery St. 12, 79013 Lviv, Ukraine*
* *Corresponding author. Tel.:* +380-32-2635174*; fax:* +380-32-2635174*; e-mail: bazylyak.liliya@gmail.com*

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This paper presents the synthesis of ternary metal NiCo-Pd nanostructures by galvanic replacement of Pd^{2+} ions on bimetallic NiCo nanoparticles (NiCo-NPs). The influence of the Pd^{2+} concentration on the kinetics of the process was investigated and it was found that the reaction rate is described by a first-order kinetic equation with respect to the concentration of Pd^{2+} and the process is controlled by diffusion. Using X-ray powder diffraction and scanning electron microscopy, it was established that the reduction of palladium ions on NiCo-NPs leads to the formation of single-crystalline nanoplates of metallic palladium with a thickness of 10-50 nm.

Ternary nanoparticles / Nickel / Cobalt / Palladium / Galvanic replacement

Introduction

Bi- and trimetallic nanostructures are promising materials for solving a wide range of applied problems in the chemical industry, in particular in catalysis, as well as in nanomaterials science. In particular, ternary nanoalloys based on transition metals are promising due to the presence of synergistic effects between their components, which increase the catalytic activity, stability, and electrical conductivity [1-3]. The combination of nickel, cobalt, and palladium in the composition of ternary nanostructures (NiCo-Pd) provides effective interaction between the components, where Ni and Co act as an active base, and Pd as a noble metal, which enhances the catalytic properties of the system [4,5].

One of the effective methods for modifying the surface of binary nanoparticles is galvanic substitution, which is based on the difference in standard electrode potentials of the metals [6]. This approach makes it possible to carry out selective deposition of a more noble metal (Pd) on the surface of a less noble one (Ni, Co) without the application of an external electric current, which ensures mild synthesis conditions and high coating uniformity. As a result of this process, a ternary nanostructure is formed, in which palladium forms surface layers or clusters on the NiCo bimetallic core, changing the electronic structure and surface properties of the system [7,8]. A detailed study of the formation processes of NiCo-Pd nanostructures, mechanisms of galvanic substitution, and interaction of the components, is necessary to optimize their properties in catalysis, electrocatalytic reactions, and energy applications. Thus, the study of the regularities of the synthesis of ternary NiCo-Pd nanostructures by galvanic replacement is of great importance for the creation of effective and economically feasible new-generation materials.

Experimental

NiCo nanoparticles (NiCo-NPs) were obtained under the following conditions: $T = 70°C$; the volume of the reaction medium was 60 mL; the water/ethylene glycol ratio was 2/1; the amount of $\nu(Ni) = \nu(Co) = 1.25$ mmol; $\nu(NaOH) = 50$ mmol; $\nu(N_2H_4) = 200$ mmol.

NiCo-Pd nanostructures were obtained by galvanic replacement in aqueous solution at 20°C in

a thermostatic reactor equipped with a magnetic stirrer, without the use of surfactants at $pH = 3$. The mass of the nanopowder of (NiCo-NPs) was 0.2 g; the volume of the $PdCl_2$ solution was 100 mL.

NiCo-Pd polymetallic nanoparticles were separated from the reaction mixture using a neodymium magnet and washed with an excess of distilled water. The obtained precipitates were dried in a desiccator under reduced pressure at room temperature.

The kinetics of the galvanic replacement were monitored by changes in the absorption spectra of the working solution using a single-beam spectrophotometer Uv/mini-1240 (Shimadzu Corp., Kyoto, Japan).

The shape and size of the metal nanoparticles were evaluated using a scanning electron microscope (SEM) EVO-40XVP (Carl Zeiss) with an energy-dispersive X-ray microanalysis system INCA Energy 350 (EDX). The size of the nanoparticles was estimated using the AxioVision V 4.8.2.0 program.

The structure and phase composition of the obtained metal nanoparticles were investigated by X-ray powder diffraction (XRD) using an Aeris-Malvern Panalytical X-ray powder diffractometer (Cu $K\alpha$ radiation, voltage 40 kV, current 15 mA, angle (2θ) 25-100°, step 0.0217°). The obtained data were analyzed by full-profile refinement according to the Rietveld method using the WinCSD software package [9].

Results and discussion

One of the most interesting and promising methods of obtaining polymetallic nanocomposites is the process of galvanic replacement of a "passive" metal on the surface of a more active metal, using the metallic nanoparticles as "sacrificial" materials. In this way, it is possible to obtain nanostructures in which the properties of the "sacrificial" metal are complemented by the properties of the deposited material. Therefore, in order to obtain ternary nanostructures based on *d*-element nanoparticles with noble metals, the method of "cementation" of palladium (Pd) ions with bimetallic NiCo nanoparticles was selected.

NiCo-NPs were synthesized in water / ethylene glycol solutions by reduction of a mixture of the corresponding hydroxides with an excess of hydrazine [10]. In general, the reduction of metal ions by hydrazine in an alkaline medium occurs in accordance with the reaction (1), which is accompanied by catalytic decomposition of hydrazine (1*a*, 1*b*) [11,12]:

$$2M(OH)_2 + N_2H_4 = 2M^0 + 4H_2O + N_2\uparrow \quad (1)$$

$$N_2H_4 \xrightarrow{M} N_2\uparrow + 2H_2\uparrow \quad (1a)$$

$$3N_2H_4 \xrightarrow{M} N_2\uparrow + 4NH_3\uparrow \quad (1b)$$

The obtained bimetallic NiCo nanopowder with an equiatomic element ratio and an average particle diameter of *ca*. 200 nm (Fig. 1, Table 1) was chosen as "sacrificial" substrate.

The influence of the initial concentration of the $PdCl_2$ solution on the rate of the process of galvanic replacement (2) was investigated. As expected, the process is fast (Fig. 2) due to the large difference in redox potentials of the half-reactions (3)-(5) and the small particle size of the sacrificial substrate.

$$NiCo + 2Pd^{2+} \rightarrow NiCo\text{-}Pd + Ni^{2+} + Co^{2+} \quad (2)$$

$$Ni^0 = Ni^{2+} + 2e^-,\ E^0 = 0.257\ V \quad (3)$$

$$Co^0 = Co^{2+} + 2e^-,\ E^0 = 0.280\ V \quad (4)$$

$$Pd^0 = Pd^{2+} + 2e^-,\ E^0 = -0.951V \quad (5)$$

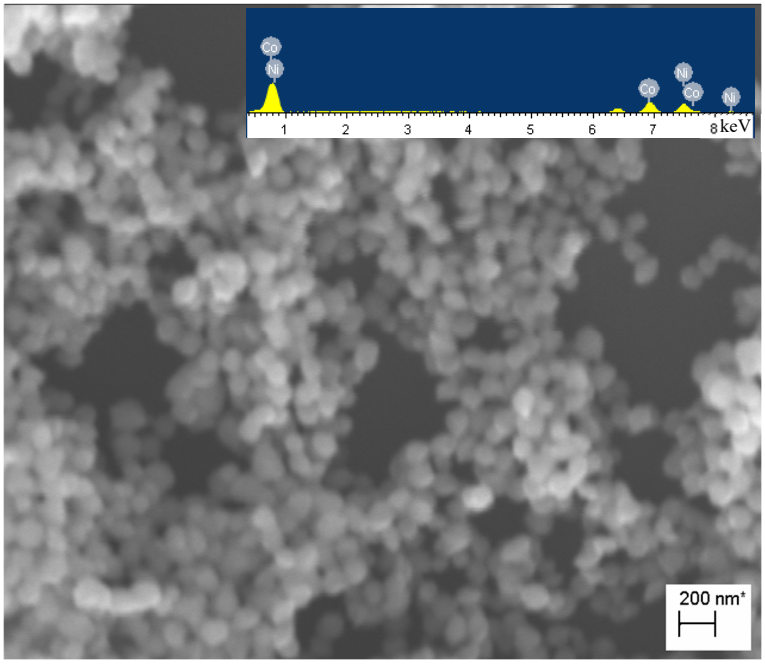


Fig. 1 SEM-image and ED-spectrum of the NiCo-NPs.

Table 1 Compositions of the obtained NiCo-NPs and NiCo-Pd.

Element	% mass			
	NiCo-NPs	NiCo-Pd (C_0 = 1 mmol/L)	NiCo-Pd (C_0 = 2.5 mmol/L)	NiCo-Pd (C_0 = 5 mmol/L)
Ni	49.3	46.8	43.8	36.9
Co	50.7	48.1	44.4	38.4
Pd	–	5.1	11.8	24.7

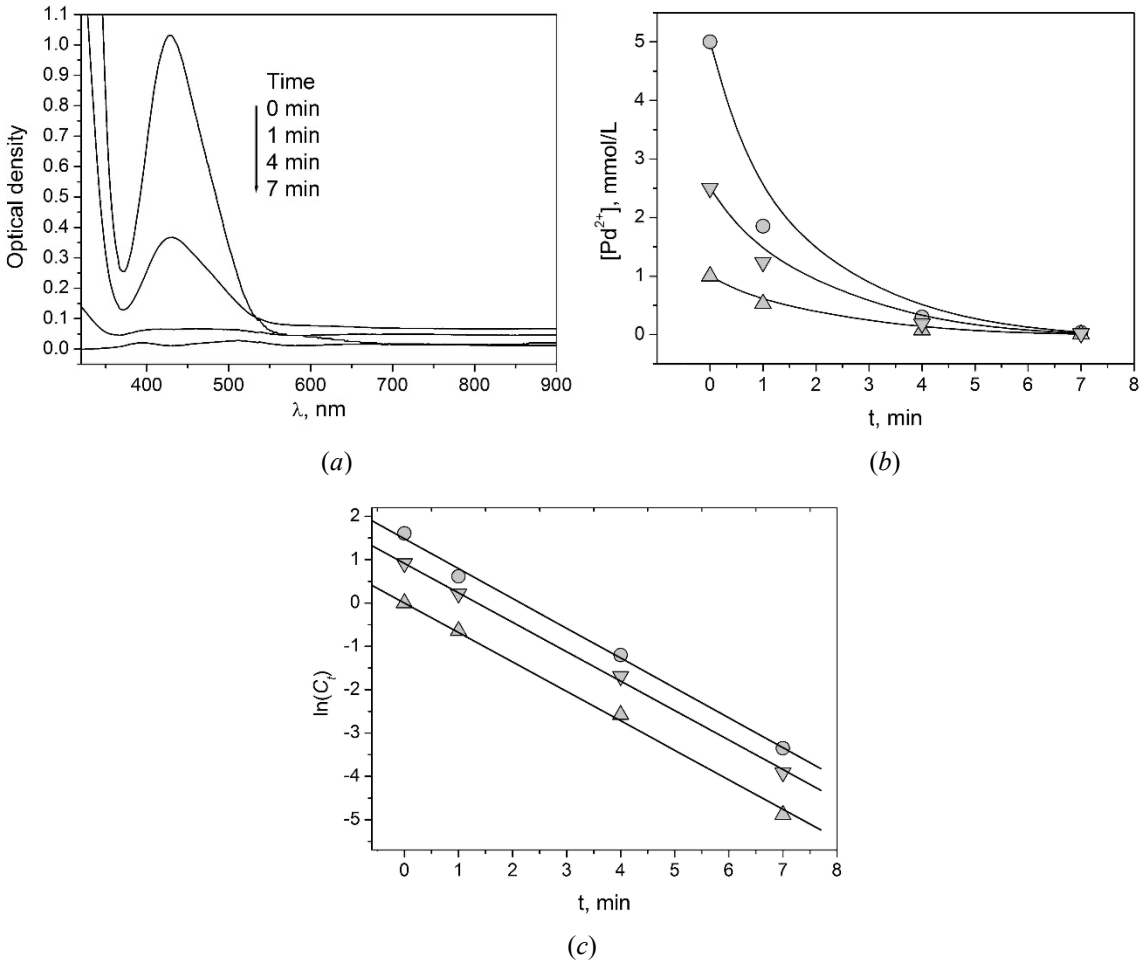


Fig. 2 Evolution of the absorption spectra of the $PdCl_2$ solution (*a*), change of the concentration of Pd^{2+} ions over time (*b*) and the kinetic curves in the coordinates of the first-order reaction (*c*).

In addition, the process occurs without an induction period, and the reaction kinetics are described by a first-order reaction equation (6).

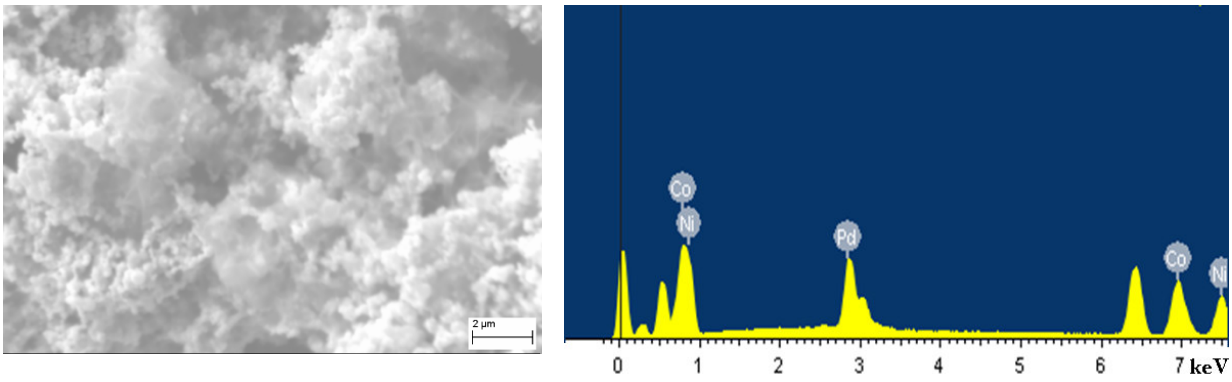
$$\ln(C_t) = \ln(C_0) - kt \quad (6)$$

Here k is the rate constant of the reaction. It was found that in all cases the values of the rate constant k are practically the same (Fig. 2(*c*)) and are equal to 0.69±0.11 min^{-1}, which indicates the diffusion nature of the process of galvanic replacement of Pd^{2+} ions on NiCo-NPs [13,14].

The resulting NiCo-Pd nanostructures were investigated using SEM (Fig. 3(*a*)) and EDX (Fig. 3(*b*)). The compositions of the obtained NiCo-Pd nanoparticles are presented in Table 1. It was established that the chemical compositions of the obtained ternary nanostructures agree with the initial compositions of the reaction mixtures.

It was found that, under the conditions of the investigation, palladium crystallized in the form of agglomerates of nanoplates of 10-50 nm thickness (Fig. 3(*a*)).

Using X-ray powder diffraction, two phases, Pd (a = 4.051(2) Å) and NiCo (a = 3.509(2) Å) with Cu-type structure, space group *Fm*-3*m*, were identified (Fig. 4). The weight fractions were 28(2)% and 72(2)% for Pd and NiCo, respectively, which is in good



(*a*) (*b*)

Fig. **3** SEM image (*a*) and ED spectrum (*b*) of NiCo-Pd nanoparticles obtained at the starting concentration of 5 mmol Pd^{2+}/L.

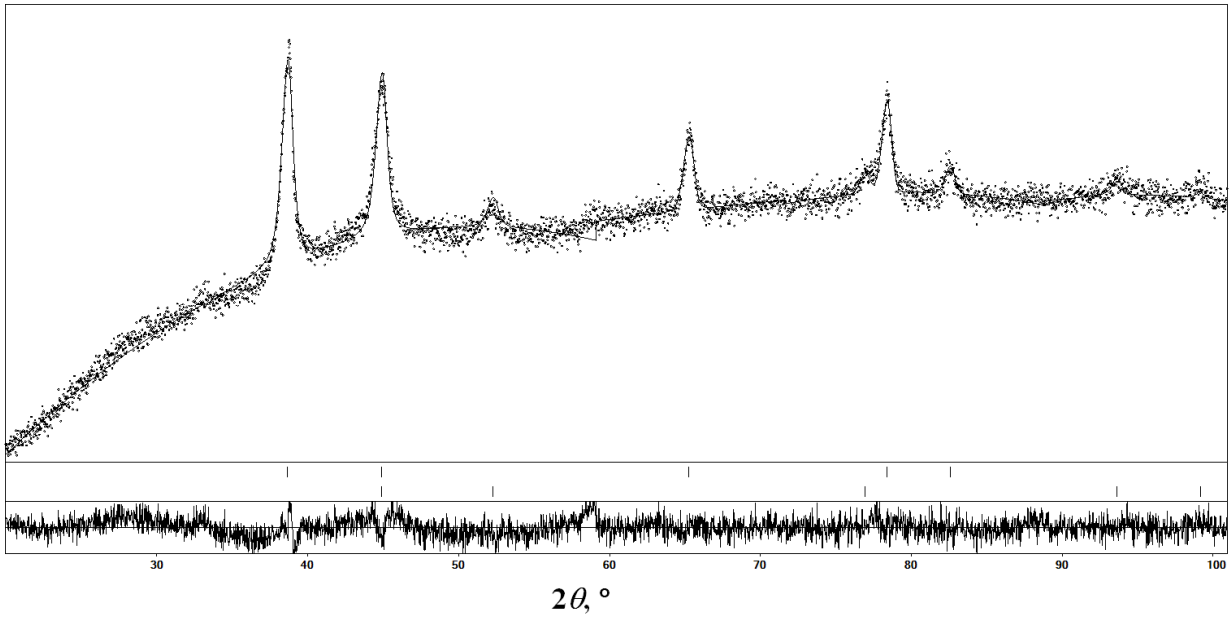


Fig. **4** XRD-pattern of NiCo-Pd nanoparticles obtained at a starting concentration of 5 mmol Pd^{2+}/L.

agreement with the elementary analysis (Table 1). There are no unidentified peaks on the XRD-pattern (Fig. 4), which indicates that the obtained nanocomposites do not contain significant amounts of impurities such as oxides / hydroxides of nickel or cobalt.

Some broadening of the peaks is observed on the XRD-pattern. Therefore, the Scherrer equation was used for the analysis of the diffraction pattern. It was found that the calculated size of the crystallites of palladium was equal to 12 nm, which is in good agreement with the SEM-observations.

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