

ТЕХНОЛОГІЯ НЕОРГАНІЧНИХ РЕЧОВИН ТА СИЛІКАТНИХ МАТЕРІАЛІВ

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PREPARING OF METALLIC ELECTROCATALYTIC NANOSTRUCTURED SURFACE BY GALVANIC REPLACEMENT METHOD (REVIEW)

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The possibilities of the galvanic replacement method in the formation of a metallic nanostructured surface for electrocatalytic processes are revealed. Based on the electrochemical mechanism of the process and taking into account the type of substrate, the following directions of application of this method are presented: synthesis of metal nanostructures and modification of metal surfaces. Among the successes in the direction of surface modification, the efficiency of deposition of nanostructured metals by galvanic replacement in the environment of organic aprotic solvents and ionic liquids has been demonstrated. The role of the medium in the controlled formation of the geometry of the metal sediment nanoparticles is noted.

Keywords: electrocatalysts, galvanic replacement, metal nanostructures, modification of the surface.

Introduction

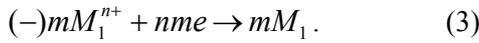
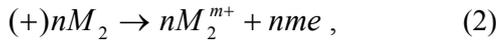
In the last decade, there is a significant expansion of the fields of application of metallic nanostructured materials. In particular, in catalysis, electronics, plasmonics, nanomedicine [1–4]. Among them, nanocatalysis (using nanoparticles of metals as catalysts) deserves special attention, as it dramatically affects synthesis of chemicals and environmental aspects of environmental protection [5, 6]. Therefore, the topical issues of modern nanotechnology are the development of highly active catalysts, which at the same time provide high selectivity and stability.

One of the effective methods for obtaining an electrocatalytic nanostructured metal surface is galvanic replacement (GR). Compared to traditional high-temperature methods (thermal evaporation, sputtering of an electron beam) galvanic replacement is characterized by moderate temperatures and, therefore, significantly lower energy costs, minimizing the use of noble metal. The method is simple to implement and provide hardware and does

not require additional reagent-reducing agents. Especially appropriate is the application of this method for the preparation of electrocatalysts based on noble metal. In view of the increased interest in such a direction of research in recent years, the purpose of the review is to analyze the current state of synthesis of metallic electrocatalytic nanostructured surfaces by galvanic replacement, the mechanism and features of such a process.

1. Theoretical aspects of galvanic replacement

The mechanism, thermodynamic and kinetic principles of galvanic replacement are thoroughly studied for macroprocesses, in particular hydro-metallurgical recovery of metals from their solutions (cementation, contact deposition). Their essence is this. GR, which can be described by the generalized equation (1), takes place by the electrochemical mechanism, which involves an electron-generating semi-reaction of oxidation of the sacrificial metal M_2 on the anode areas (2) and a half-reaction of metal M_1 recovery on the cathode areas (3).



Synthesis of nanostructures by the method of galvanic replacement has certain features due, first of all, to nanosized effect, low concentration of metal ions in solutions, high surface energy, which results in significant rates of dissolution of the substrate and metal recovery, practical absence of the induction period [5, 7]. In addition, the area of the anode and cathode regions, that is, the local sections of the course of electrochemical and chemical processes, are lower than those of the classical hydrometallurgical processes of cementation.

According to the thermodynamic principles of processes, the galvanic replacement is possible if the value of the change in the Gibbs energy, as well as for any chemical reaction, is less than zero. For electrochemical processes

$$-\Delta G = nF\Delta E = nF(E_{M_1^{n+}/M_1} - E_{M_2^{m+}/M_2}), \quad (4)$$

where ΔE – electromotive force of the process; F – the constant of Faraday; n – number of electrons involved in the process; $E_{M_1^{n+}/M_1}$, $E_{M_2^{m+}/M_2}$ – equilibrium potentials.

The self-propelled flow of galvanic replacement is possible if this condition is maintained

$$-\frac{\Delta G}{nE} = (E_{M_1^{n+}/M_1} - E_{M_2^{m+}/M_2}) > 0. \quad (5)$$

Therefore, galvanic replacement occurs if the equilibrium potential of oxidation of $E_{M_2^{m+}/M_2}$ metal-reducer $< E_{M_1^{n+}/M_1}$ recoverable metal. In general, such a process is spontaneous, which complicates the controlled formation of the sediment morphology and the geometry of its individual particles. The rate of electrochemical reactions in the anode and cathode regions depends on many factors, namely: the nature of the substrate or sacrificial template; the nature of the deposited metal; composition of the solution; stable activity of the anode surface; temperature and duration of substitution [7]. Accordingly, the process of forming nanoparticles on the surface of the restoring substrate (Fig. 1, a) or the sacrificial template (Fig. 1, b) and the growth of the metal sediment is multifactorial.

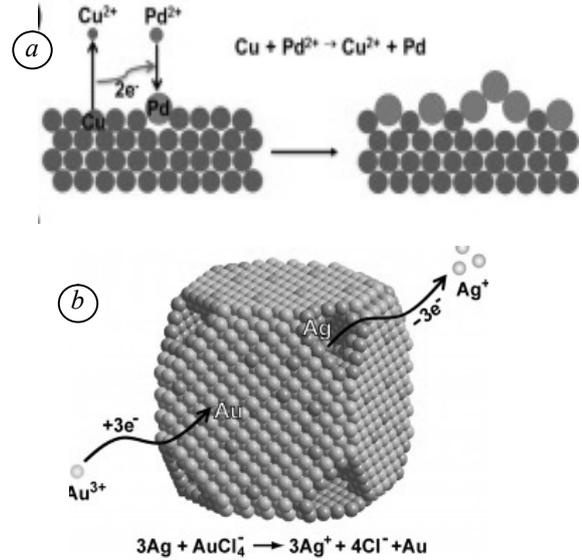


Fig. 1. Scheme for the formation of nanoparticles by the method of galvanic replacement on the surface of the substrate reducer (a) [8] and sacrificial template (b) [9]

2. Methods of forming an electro-catalytic surface using a galvanic replacement

Materials used as electrocatalysts are formed on a conductive or semiconducting basis. Today, electrocatalysts based on nanostructured metal systems of GR are prepared by the following two methods: 1) galvanic substitution directly on the metal surface of the electrode; and 2) fixation to the surface of the electrodes of the pre-synthesized nanostructures by the GR method.

In fundamental researches, which focused on the establishment of the mechanism of the method, as well as the study of morphology and interaction between components of the multimetal system, materials such as substrates for electrodes are used: glassy carbon (GC) [10, 11], single crystals of gold and ruthenium [12, 13], polycrystalline titanium and gold [14, 15]. In this case, galvanic replacement by the first method is carried out directly on the block metal (copper plates or foil, porous nickel, etc.) or on pre-electrochemically deposited metal (copper on graphite or GC, nickel on a glassy carbon or on copper, etc.). Below we consider the features of nanostructured catalysts obtained by galvanic replacement on the conductive substrate surface or sacrificial template.

2.1. Modification of the substrate surface

Modification of the surface by nanostructures is considered in the aspect of obtaining electrocatalysts by the method of galvanic replacement directly on the material-basis (Table 1).

Table 1

Conditions for the formation of metal nanoparticles (M_1 NPs) on the surface of the substrate metal (M_2) by galvanic substitution and their use in electrocatalysis

M_2	M_1 NPs	Precursors	t, °C	τ	Particle size, nm	Electrocatalys in process	Ref
Cu	Pt, Pd	4.0 mM H_2PtCl_6 4.0 mM $PdCl_2$	22±2	25 min	40–50	oxidation of glycerol	[16]
Cu	Ag	1. 5. 10. 20 mM $AgNO_3$	22±2	10 min	100	hydrogen peroxide electroreduction	[17]
Cu	Au	5 mM $AuCl_4$	22±2	1–5 min	100	nitrate reduction	[18]
Cu	Pt, Pd	$PdCl_2$, $PtCl_4$ y 0.1 M $HClO_4$.	22±2	15 min	100	hydrogen evolution	[19]
Ag	Pd	2 mM $PdSO_4$ + 0.5 M H_2SO_4	22±2	20 min	100	$HCOOH$ oxidation	[20]
Ag	Au	12.5 mM $HAuCl_4$	11	6–75 min	100–200	CO_2 reduction	[21]
Ni	Ir	1 mM K_2IrCl_6	65	15 min	100	oxygen Evolution	[22]
Ni	Pd	0.2 mM $PdCl_2$	80	10 hours	1–5	methanol oxidation	[23]
Ni	Pd, Ag	20 mM $AgNO_3$ 25 mM K_2PdCl_4	22±2	10 min	–	methanol oxidation	[24]
Zn	Pt	30 % $NaOH$ + 1 mM H_2PtCl_6	22±2	48 hours	60–70	methanol oxidation	[25]

The application to a metal surface of a nanostructural precipitate of another metal or bimetal leads to the formation of a metal/lining system, which is characterized by new functional properties.

In addition to the above materials, as a surface (substrate-reductant), metals M_2 with positive values of standard electrode potentials are used – copper [16–19], silver [20, 21] and negative – nickel [22–24], zinc [25]. Due to the “generated” electrons on such a surface, a precipitate of a catalytically active metal M_1 with a more positive standard potential is formed – Pt [16, 19, 25], Pd [16, 19, 20, 23], Au [18, 21], Ag [17, 24], Ir [22]. Modern studies are aimed at studying the dependences of the morphology of deposited metal on the substrate surface and, accordingly, the electro-catalytic properties of the system obtained from the main factors of the galvanic replacement process.

Modification of copper surface

The surface of copper modified with silver, gold, palladium and platinum is characterized by elevated electro-catalytic activity. Copper is an affordable and cheap foundation for the application of noble metal nanoparticles. For galvanic

replacement, copper, electrochemically deposited from acidic sulfate electrolytes, which is characterized by a developed and porous surface, is predominantly used [17–19].

Modification of copper surface with silver is carried out mainly in aqueous solutions by the galvanic replacement reaction (6).



The morphology of heterogeneous nanostructures formed on the copper surface is significantly dependent on the galvanic replacement parameters. In particular, the concentration of Ag^+ ions greatly affects the formation and growth of Ag/Cu nanodendrites [17]. The analysis of typical SEM images of Ag/Cu nanostructures obtained over a fixed time of galvanic substitution indicates that an increase in the concentration of $AgNO_3$ (1–20 mM) results in a change in morphology from lamellar (lamellar) to branched dendritic with an increase in the size of their structural particles (Fig. 2). The duration of the galvanic replacement slightly affects the morphology of the silver precipitate. The

reduction peak potential of hydrogen peroxide was about -0,25 V (vs. a saturated calomel electrode), which indicated that the assynthesised Ag/Cu dendrites had favourable electroreduction activity towards hydrogen peroxide.

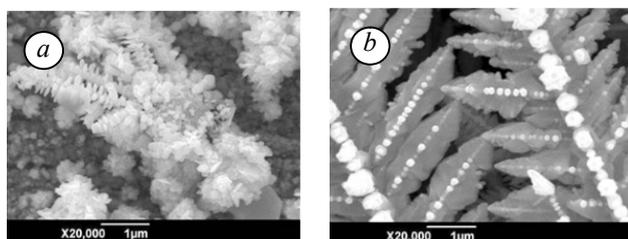
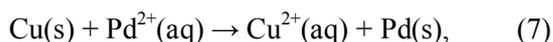


Fig. 2. SEM images of Ag–Cu nanostructures obtained at different concentrations Ag^+ ion (mM): a – 1, b – 20 [17]

The method of galvanic replacement makes it possible to modify the surface with mono- and bimetal systems. Thus the authors [19] proposed the production of bimetal electrocatalysts Pd-Pt/Cu. The Cu nanofoam was used as a substrate to reduce Pd(II) and Pt(IV) ions to metal form at the surface of electrode at open circuit voltage. The standard reduction potentials of Pd^{2+}/Pd and Pt^{4+}/Pt pairs are 0.83 V and 0.74 V vs. the standard hydrogen electrode (SHE). These standard potentials are positive of that for Cu^{2+}/Cu , 0.34 V vs. SHE, so the below galvanic replacement reactions are thermodynamically favorable:



Testing of the electro-catalytic properties of the obtained bimetal system Pd-Pt/Cu showed its higher activity than pure platinum, as evidenced by a half times the value of current density and displacement of the potential of the beginning of the hydrogen evolution reaction to a more positive value (Fig. 3).

In addition, such a catalyst has a significantly lower cost due to a decrease in the mass fraction of platinum. In particular, the best performance is observed for the Pd65Pt35 catalyst. The coprecipitation Pd and Pt amplify the electrocatalytic action by an electronic effect. Chronoamperometric (CA) studies of bimetal catalyst showed its stability in time (the current does not decrease even after 1000 s) (Fig. 4).

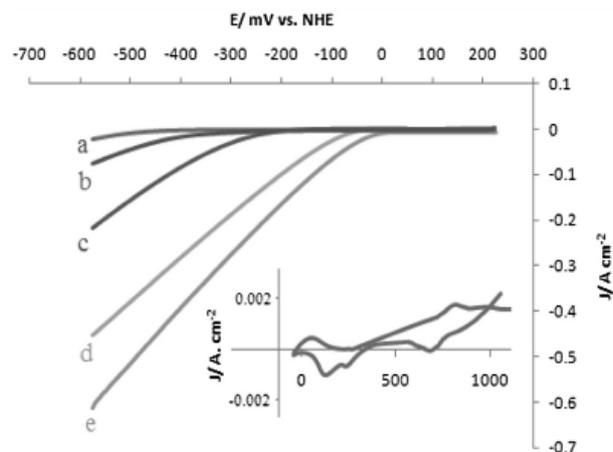


Fig. 3. Linear sweep voltammetry of (a) bare Cu electrode, (b) Cu nanofoam electrode, (c) Pd, (d) Pt, (e) Pd65Pt35 in 0,5 M H_2SO_4 solution. Inset: Cyclic voltammograms recorded for Pd65Pt35 in 0.5 M H_2SO_4 solution [19]

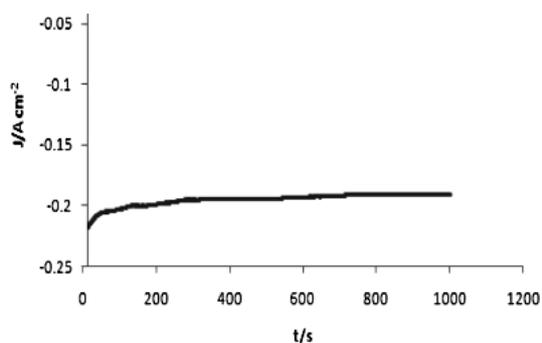


Fig. 4. CA curve for HER catalyzed by the Pd65Pt35 at 250 mV vs. NHE in 0.5 M H_2SO_4 solution [19]

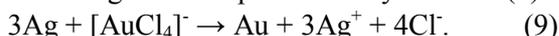
Modification of the silver surface

The surface of electrolytically deposited silver and modified catalytically active metals Pd [20], Au [21] has a predominant application for the oxidation of formic acid and the recovery of carbon dioxide. It is shown [20] that galvanic replacement does not provide the formation of a continuous layer of palladium on the silver surface, since Ag atoms are embedded in a surface layer at the top of Pd^0 and can not be substituted by Pd^{2+} . In addition, this is due to the peculiarity of the process of galvanic replacement, in particular the need for activity of at least the minimum number of anode sections.

Stationary polarization curves in a solution of 0.5 M H_2SO_4 + 0.5 M HCOOH show a high specific activity for Pd/Ag composites, which is almost on the order of magnitude higher than palladium in the range of potentials of 0.10–0.25 V. Such effects of

palladium The authors explain both the inhibition of formed chemisorbed compounds and the development of new active centers at the boundary of Pd/Ag.

Particularly high electrocatalytic activity is characterized by porous golden films (Fig. 5). The thickness and roughness of the surface of porous gold films can be controlled by adjusting the duration of the galvanic replacement by reaction (9)



At low overvoltage (390 mV), the porous film exhibits significantly higher activity (about 40 times) than the polycrystalline analogue [21]. This is due to highly developed nanostructured surface.

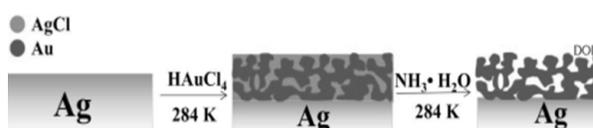


Fig. 5. Schematic illustration of the key steps for fabricating porous gold films [21]

By changing the thickness of the golden nanoporous film, it is possible to adjust the efficiency of the electrocatalytic conversion of CO₂ to CO, reaching a maximum of 90.5 % (Fig. 6).

Modification of the surface of nickel

Electrodescent nickel on glassy carbon electrodes [22] or nickel foam (a specially prepared substrate) used as the basis for the formation of a catalytically active nickel surface [24].

The enhanced catalytic activity is characterized by electrodes IrO₂-Ir/Ni obtained by galvanic replacement of nickel layers with an iridium followed by anodization of the obtained system (Fig. 7). Prepared electrodes IrO₂-Ir/Ni have been tested as anode for oxygen recovery (OER) from acid solutions. It has been found that they exhibit significantly higher catalytic activity compared to the usual IrO₂ oxide film, anode formed on block iridium [22].

The binary electrocatalysts Pd-Ag/Ni have been obtained by the method of gradual electroplating of the nickel surface [24]. The inclusion of Pd and Ag in the substrate of nickel “foam” greatly increases its activity in electrocatalytic oxidation of methanol. This is due to the synergistic effect between Pd and Ag in the formed nanostructured Pd-Ag alloy. In addition, the Pd-Ag/Ni activity is significantly dependent on the quantitative correlation between Pd and Ag, which is governed by the duration of substitution. Among the

investigated Pd-Ag/Ni electrocatalysts, the Pd55Ag45/Ni “foam” exhibits the highest activity in relation to the oxidation of methanol in alkaline medium: 2.8 and 3.3 times as compared to Pd/Ni. In addition, cooked “foam” Pd55Ag45/Ni has a high wear resistance in electrooxidation methanol. The efficiency of binary systems indicates the high potential of their use in electrocatalytic processes.

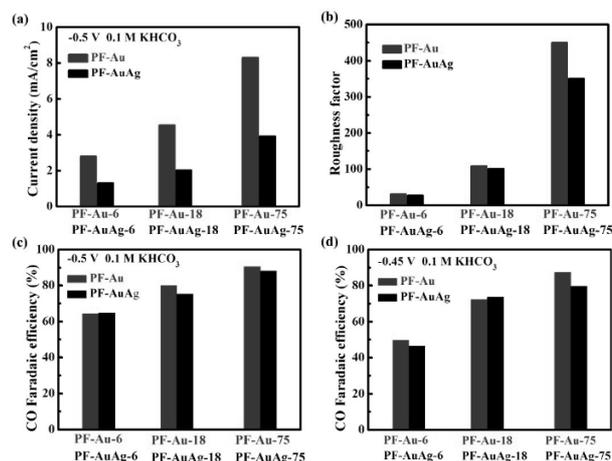


Fig. 6. Comparison of electrocatalytic performance of Au and AuAg electrodes: (a) current density, (b) CO Faradaic efficiency at -0.5 V, (c) CO Faradaic efficiency at -0.45 V measured in CO₂-saturated 0.1 M KHCO₃ [21]

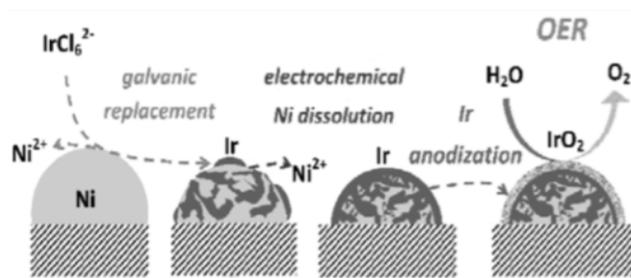


Fig. 7. Scheme for the formation of catalytically active electrodes IrO₂-Ir/Ni [22].

2.2. Synthesis of nanostructures on a sacrificial nanotemplate

The obtaining of a metal electrocatalytic nanostructured surface in the absence of a substrate material involves the synthesis of nanostructures on the sacrificial nanosilver (M₂NPs), followed by their application to the conductive base of the electrode. Conditions for the formation of nanoparticles of metals on the surface of a metal-nanoparticle by a method of galvanic replacement and their use in electrocatalysis are given in Table 2. Galvanic replacement is mainly obtained by hollow nanostructures and core@shell structures.

Conditions for the formation of nanoparticles of metals (M_1 NPs) on the surface of metal-nanoparticle (M_2 NPs) galvanic substitution and their use in electrocatalysis

M_2 NPs	M_1 NPs	Precursors	t, °C	τ	Particle	Electrocatalys in process	Ref
Ag	Pt	K_2PtCl_4	22±2	24 hours	20	hydrogen evolution	[26]
Cu	Pt	10 mM K_2PtCl_4	22±2	60 min	2–3	oxygen reduction and	[27]
Cu	Pt	5 mM K_2PtCl_6 +	22±2	45 min	20–30	methanol oxidation	[28]
Cu	Pt	0.05 mM	220	90 min	5	methanol oxidation	[29]
Cu	Pt, Ru	0.05 mM $Pt(acac)_2$.	220	90 min	5	methanol oxidation	[29]
Cu	Pt	2 mM K_2PtCl_4 .	22±2	20 min	1–4	methanol oxidation	[30]
Cu	Pt	10 mM K_2PtCl_6	22±2	35–40	4	oxygen reduction and	[31]
Cu	Pt	1mM K_2PtCl_6	22±2	45 min	3–5	methanol oxidation	[32]
Cu	Au	0.075 mM	140	20 min	5	CO ₂ reduction	[33]
Cu	Pd	4.5 mM $PdCl_2$	22±2	60 min	20–40	ethanol oxidation	[34]
Ni	Pd	10 mM $PdCl_2$	22±2	5–720	30–50	methanol oxidation	[35]
Ni	Pt	0.5 M H_2PtCl_6	22±2	120 min	25–30	ethanol oxidation	[36]
Co	Pt	2 mM K_2PtCl_4	22±2		4.70	oxygen reduction	[37]
Co	Pt	25–250 mg/l	22±2	72 hours	20–40	oxygen reduction	[38]

The method of galvanic replacement as a controlled synthesis of mono- and bimetal hollow nanomaterials is most studied for Ag/Pt [26], Cu/Pt [27–32], Cu/Au [33], Cu/Pd [34], Ni/Pd [35], Ni/Pt [36], Co/Pt [37, 38]. The template for the synthesis of hollow nanostructures is predominantly stabilized nanoclusters of copper, silver, and nickel.

In the process of synthesis of hollow nanostructures nanostructures by galvanic replacement, the main characteristic of the finite structure is the shape or morphology of the transformed matrix. Therefore, to ensure that the template's configuration is adhered to by the finite nanostructure, the atoms of the recovered metal must settle on its surface. In the replacement reactions, the complete removal of the less active sacrificial template is usually not achieved, and its residual presence can substantially affect the electro-catalytic properties of the end material. Thus, the Pt/Ag system is used as an electro-catalytic electrode in fuel cells. However, in many cases, certain Ag content remains, which affects the properties of nanomaterial [26].

The core@shell structures can be synthesized by galvanic replacement provided that only the porous shell is formed on the surface of the nucleus. This is due to the feature of the process, in particular the need for openness of the minimum number of anode sections. In the nanostructures of Me@Pt(Pd),

catalytic properties are usually determined by the shell of Pt(Pd) on the surface in the form of a monolayer. Therefore, such structures are much more advantageous, because they reduce the costs and increase the catalytic activity of the initial nanostructure [34, 39].

The unique core@shell Au@Pd nanoparticles (Fig. 8) exhibit increased electrocatalytic activity in the oxidation of formic acid, electrochemical stability and long-term durability as a result of the enhanced coupling between the Au nucleus and the Pd shell [39]. Synthesis of nanoparticles was carried out by the galvanic replacement of Cu on Pd on hollow nanoparticles Au. The nucleus of gold in this structure plays a crucial role for the donation of electrons and stabilization of the Pd shell. The highest catalytic properties have revealed the nanostructures Au@Pd20 due to the optimal effect of electronic clutch.

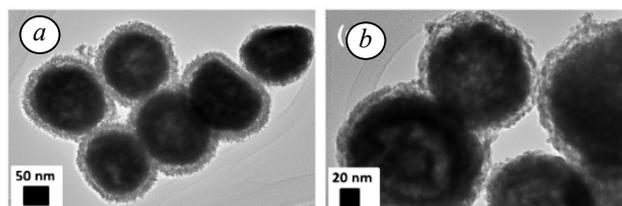


Fig. 8. TEM images of (a) Au@Pd20, (b) Au@Pd40 [39]

Authors [28] proposed the production of metal catalysts by galvanic replacement of copper nanoparticles in an acidic solution of K_2PtCl_6 . Analysis of the atomic ratio Pt:Cu of the resulting system showed that the degree of modification of platinum is not more than 37%. Moreover, platinum is concentrated in the outer part of copper nanostructures. Synthesized Pt-Cu nanoparticles of 20–30 nm (Fig. 9) were applied to a carbon base with a large surface area. The resulting Pt-Cu/C system is tested as oxidation electrodes of carbon oxide (II) and methanol. The test results showed their benefits with Pt/C analogues in the area of the electrically active surface. However, due to the agglomeration of Pt-Cu/C particles, this system is inferior to Pt/C by specific mass.

Noble metals are deposited by galvanic replacement and on complex copper surfaces. Thus, the paper [29] shows the possibility of forming bi- and trimetallic nanostructures (CuPt, CuPtRu) on copper nanotubes. It is established that high concentration of salts of noble metals leads to excessive growth of ultradispersed, dispersed or branched structures on the surface of 1D nanostructures.

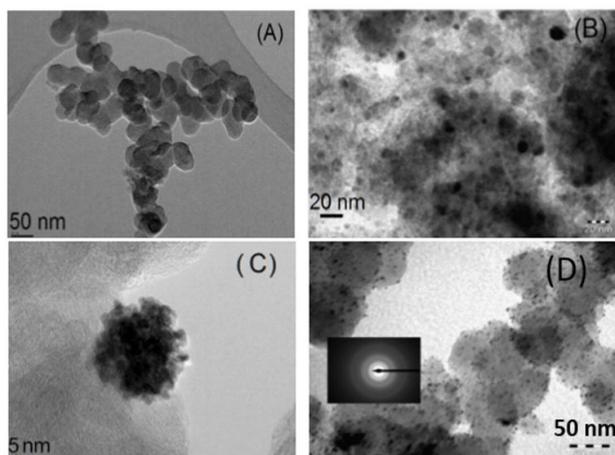


Fig. 9. TEM micrographs of Pt(Cu) particles supported on carbon particles (Pt(Cu)/C); (A), (B), (C) micrographs at different magnifications as indicated by the scale bars. For comparison, a micrograph for commercial 20% w/w Pt/C catalyst is shown in (D) [28]

Accordingly, the roughness of the surface and its composition can be adjusted by varying the concentrations of the recovered metals. In particular, for 0.05 mM $Pt(acac)_2$ and 0.08 mM $RuCl_3$, CuPt and CuPtRu ~ 5 nm nanoparticles are obtained (Fig. 10). The electrochemical reactivity is influenced not only by surface roughness (particle size), but

also by the composition of the surface (content Pt). The trimetallic CuPtRu nanostructures improve the stability of the catalyst in the acidic medium.

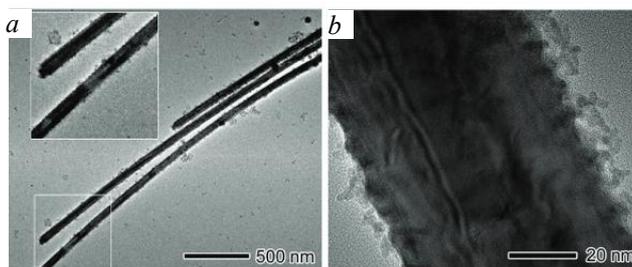


Fig. 10. Characterization of CuPtRu 1D nanostructures with small-branch-decorated rough surfaces (sr-CuPtRu): a – TEM image with an inset of the zoom-in view of the box in white; b – HRTEM image [29]

One of the activating factors of galvanic replacement, namely the anode sections, is the use of ultrasound. Under these conditions, Pd@Cu nanostructures (20–40 nm) are synthesized and an electrocatalyser is formed that has a large number of active Pd centers and a large surface area. The catalyst Pd@Cu has demonstrated a synergistic catalytic effect on the oxidation of ethanol with a current density that is 9.5 times greater than commercial Pd/C. In addition, thermodynamic and kinetic studies have shown that the Pd@Cu catalyst is characterized by a low energy barrier and high charge transfer velocity in the direction of ethanol oxidation [34].

3. Perspective directions of galvanic replacement in catalysis

As stated above, the galvanic replacement method is an extremely versatile approach for the production of catalytically active nanostructured materials. However, most studies are limited to substituting metallic nanoparticles or metal surfaces in aqueous solutions. This causes the course of side effects on the electrode sections and in the reaction medium. Accordingly, certain difficulties arise in the controlled synthesis of nanostructured precipitates. Such side effects are the electrical reduction of hydrogen, which can significantly affect the growth of nanoparticles. In addition, the pH increases in near-surface layers, which violates the given acidity of the working solution [7].

In order to reduce and avoid the flow of such undesirable processes in the last decade, there is

interest in the study of galvanic replacement in the environment of organic solvents, in particular aprotic – DMF, DMSO [7, 40–42].

Polar molecules DMF or DMSO (L) due to higher, compared with water molecules, electrodonor properties are formed with ions of reducing metals solvate, for example, $[\text{AgL}_m]^+$, $[\text{NiL}_n]^{2+}$, $[\text{PdL}_p]^{2+}$. The latter determine cathode polarization, which affects the formation of the geometry of nanoparticles. In addition, due to the formation of surface complexes on the latter under the donor-acceptor mechanism $\text{M} \rightleftharpoons \text{L}$ the effect of molecules of aprotic solvents is similar to that of surfactants.

One of the promising directions of the catalytically active nanostructured materials is galvanic replacement in ionic liquids [43]. In aqueous solutions, the reaction of galvanic replacement substitution occurs at the oxidation-reduction potentials of the standard electrochemical series. For comparison, in the case of ionic liquids, the reaction of GR can be initiated by the formation of complexes of metal ions with anions of ionic liquids. Therefore, oxidation-reduction potentials in ionic liquids may differ significantly from those for metal complexes in aqueous solutions. The main advantage of the galvanic replacement substitution in ionic liquids is their much higher conductivity, since they consist entirely of cations and anions. However, compared with aqueous solutions for ionic liquids there is no single electrochemical series due to the lack of a universal electrode for comparison. Depending on the characteristics of the individual experiment, the electrode Pt is most suitable. It is shown that the nature of the ionic liquid, the concentration of metal ions, pH and temperature affect the morphology of the reducing metals, the size of the particles, as well as the rate of deposition. The nature of the ionic liquid also affects the crystallographic planes. An example is the deposition of gold nanoparticles and platinum from various ionic liquids. Thus, depending on the salt of Au and Pt and the ionic liquid, precipitates of various sizes and geometric shapes, in particular triangular gold nanoplasts, are formed [43]. It is shown that the efficiency of the electrocatalytic oxidation of formic acid depends on the morphology of the synthesized nanoparticles. Therefore, galvanic replacement in ionic liquids has a huge potential for the development of functional materials for electrocatalysis.

Conclusions

The analysis of literature sources regarding the current state of synthesis of a metal electrocatalytic nanostructured surface has shown that one of the perspectives of the methods of its obtaining is galvanic replacement. Such a method is easy to implement and provide hardware and at the same time universal for controlled formation of a catalytically active surface. The conditions of galvanic replacement can be regulated by the dimension and morphology of the metal sediment and, accordingly, the electrocatalytic properties of the electrodes on their basis. The main directions of preparation of electrocatalysts based on nanostructured metal systems obtained by galvanic replacement are: 1) substitution directly on the metal surface of the electrode; 2) fixation to the electrode surface of pre-synthesized nanostructures. Aprotic organic solvents and ionic liquids can be used as an environment for controlling the morphology of nanoparticles of a metallic precipitate during electroplating and, accordingly, the effectiveness of electrocatalytic reactions.

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References

1. Yae, S., Morii, Y., Fukumuro, N., Matsuda, H. (2012). Catalytic activity of noble metals for metal-assisted chemical etching of silicon. *Nanoscale Research Letters*, 7, 352.
2. Chen, L., Jing, Q., Chen, J., Wang, B., Huang, J., Liu, Y. (2013). Silver nanocrystals of various morphologies deposited on silicon wafer and their applications in ultrasensitive surface-enhanced Raman scattering. *Materials characterization*, 85, 48-56.
3. Russo, L., Merkoci, F., Patarroyo, J., Piella, J., Merkoç, A., Bastus, N. G., Puntès, V. (2018). Time- and Size-Resolved Plasmonic Evolution with nm Resolution of Galvanic Replacement Reaction in AuAg Nanoshells Synthesis. *Chemistry of Materials*, 30, 5098-5107.
4. Katas, H., Moden, N. Z., Lim, C. S., Celesistinus, T., Chan, J. Y., Ganasan, P., Abdalla, S. (2018). Biosynthesis and Potential Applications of Silver and Gold Nanoparticles and Their Chitosan-Based Nanocomposites in Nanomedicine. *Journal of Nanotechnology*, 4290705, 13.

5. Papaderakis, A., Mintsouli, I., Georgieva, J., Sotiropoulos, S. (2017). Electrocatalysts Prepared by Galvanic Replacement. *Journal of Catalysis*, 80, 34.
6. Reis Machado, A. S., Nunes da Ponte, M. (2018). CO₂ capture and electrochemical conversion. *Green and Sustainable Chemistry*, 11, 86-90.
7. Кунтий, О. І. (2008). *Електрохімія і морфологія дисперсних металів*. Монографія. Львів: НУ "ЛІП", 208.
8. Zhang, X., Zhou, Y., Zhang, B., Zhan, J. (2017). An improved galvanic replacement deposition method for synthesis of compact palladium coatings on copper substrates. *Materials Letters*, 15, 75-78.
9. Xia, X., Wang, Y., Ruditskiy, A., Xia, Y. (2013). 25th anniversary article: galvanic replacement: a simple and versatile route to hollow nanostructures with tunable and well-controlled properties. *Advanced Materials*, 25, 6313-6333.
10. Papaderakis, A., Pliatsikas, N., Prochaska, C., Papazisi, K. M., Balomenou, S. P., Tsiplakides, D., Patsalas, P., Sotiropoulos, S. (2014). Ternary Pt-Ru-Ni catalytic layers for methanol electrooxidation prepared by electrodeposition and galvanic replacement. *Frontiers in Chemistry*, 2, 29.
11. Papaderakis, A., Pliatsikas, N., Prochaska, C., Vourlias, G., Patsalas, P., Tsiplakides, D., Balomenou, S., Sotiropoulos, S. (2016). Oxygen evolution at IrO₂ shell-Ir-Ni core electrodes prepared by galvanic replacement. *The Journal of Physical Chemistry C*, 120, 19995-20005.
12. Brankovic, S. R., Wang, J.X., Adži'c, R. R. (2001). Metal monolayer deposition by replacement of metal adlayers on electrode surfaces. *Surface Science*, 474, L173-L179.
13. Brankovic, S.R., McBreen, J., Adži'c, R. R. (2001). Spontaneous deposition of Pt on the Ru(0001) surface. *Journal of Electroanalytical Chemistry*, 503, 99-104.
14. Kokkinidis, G., Stoychev, D., Lazarov, V., Papoutsis, A., Milchev, A. (2001). Electroless deposition of Pt on Ti: Part II. Catalytic activity for oxygen reduction. *Journal of Electroanalytical Chemistry*, 511, 20-30.
15. Van Brussel, M., Kokkinidis, G., Hubin, A., Buess-Herman, C. (2003). Oxygen reduction at platinum modified gold electrodes. *Electrochimica Acta*, 48, 3909-3919.
16. Rezaei, B., Saeidi-Boroujeni, S., Havakeshian, E., Ensafi, A. A. (2016). Highly efficient electrocatalytic oxidation of glycerol by Pt-Pd/Cu trimetallic nanostructure electrocatalyst supported on nanoporous stainless steel electrode using galvanic replacement. *Electrochimica Acta*, 203, 41-50.
17. Kang, Y., Chen, F. (2013). Preparation of Ag-Cu bimetallic dendritic nanostructures and their hydrogen peroxide electroreduction property. *Journal of Applied Electrochemistry*, 43, 667-677.
18. Balkis, A., Crawford, J., O'Mullane, A. P. (2018). Galvanic Replacement of Electrochemically Restructured Copper Electrodes with Gold and Its Electrocatalytic Activity for Nitrate Ion. *Nanomaterials*, 8, 756.
19. Rezaei, B., Mokhtarianpour, M., Ensafi, A. (2015). Fabricated of bimetallic Pd/Pt nanostructure deposited on copper nanofoam substrate by galvanic replacement as an effective electrocatalyst for hydrogen evolution reaction. *Hydrogen energy*, 1-9.
20. Podlovchenko, B. I., Maksimov, Yu. M., Maslakov, K. I., Volkov, D. S., Evlashin, S. A. (2017). Galvanic displacement and electrochemical leaching for synthesizing Pd-Ag catalysts highly active in FAOR. *Electroanalytical Chemistry*, 788, 217-224.
21. Chena, C., Zhangb, B., Zhongb, J., Cheng Z. (2017). Selective electrochemical CO₂ reduction over highly porous gold films. *Materials Chemistry A*, 5, 21955-21964.
22. Papaderakis, A., Prochaska, C., Pliatsikas, N., Patsalas, P. (2016). Oxygen Evolution at IrO₂ Shell-Ir-Ni Core Electrodes Prepared by Galvanic Replacement. *The Journal of Physical Chemistry C*, 120, 19995-20005.
23. Rong, Z. J., Zhang, Q., Siwal, S. S. (2019). *Galvanic Replacement-Mediated Synthesis of Ni-Supported Pd Nanoparticles with Strong Metal-Support Interaction for Methanol Electro-oxidation*. *Small*.
24. Niu, X., Xiong, Q., Li, X., Zhang, W. (2017). Incorporating Ag into Pd/Ni Foam via Cascade Galvanic Replacement to Promote the Methanol Electro-Oxidation Reaction. *Journal of The Electrochemical Society*, 164, 651-657.
25. Hosseini, G., Abdolmaleki, M., Daneshvari Esfahlan, V. (2017). Porous Co/Co-Ni-Pt nanostructures prepared by galvanic replacement towards methanol electro-oxidation. *Porous Materials*, 24, 305-313.
26. Bansal, V., O'Mullane, A. P., S.K. Bhargava, S. K. (2009). Galvanic replacement mediated synthesis of hollow Pt nanocatalysts: Significance of residual Ag for the H₂ evolution reaction. *Electrochemistry Communications*, 11, 1639-1642.
27. Li, Q., Wu, G., Xu, P., Zhao, H. (2013). Self-supported Pt nanoclusters via galvanic replacement from Cu₂O nanocubes as efficient electrocatalysts. *Nanoscale*, 5, 7397-7402.
28. Mintsouli, I., Georgieva, J., Papaderakis, A., Armanyanov, S. (2016). Methanol oxidation at platinumized copper particles prepared by galvanic replacement. *Journal of Electrochemical Science and Engineering*, 6(1), 17-28.
29. Mathurin, L. E., Benamara, M., Tao, J., Zhu, Y. (2018). Tailoring the Surface Structures of CuPt and CuPtRu 1D Nanostructures by Coupling Coreduction with Galvanic Replacement. *Particle Systems Characterization*, 35.

30. Mintsouli, I., Georgieva, J., Armyanov, S., Valova, E. (2013). Pt-Cu electrocatalysts for methanol oxidation prepared by partial galvanic replacement of Cu/carbon powder precursors. *Catalysis B: Environmental*, 136-137, 160–167.
31. Podlovchenko, B. I., Krivchenko, V. A., Maksimov, Y. M., Gladysheva, T. D. Specific features of the formation of Pt(Cu) catalysts by galvanic displacement with carbon nanowalls used as support. *Electrochimica Acta*, 76, 137-144.
32. Geboes, B., Mintsouli, I., Wouters, B., Georgieva, J. (2014). Surface and electrochemical characterisation of a Pt-Cu/C nano-structured electrocatalyst, prepared by galvanic displacement. *Applied Catalysis B: Environmental*, 150-151, 249-256.
33. Zhou, J., Lan, D., Yang, S., Guo, Y. (2018). Thin-wall hollow Au-Cu nanostructures with high efficiency in electrochemical reduction of CO₂ to CO. *Inorganic Chemistry Frontiers*, 5, 1524-1532.
34. Farsadrooh, M., Noroozifar, M., Modarresi-Alam, A., Saravani, H. (2019). Sonochemical synthesis of high-performance Pd@CuNWs/MWCNTs-CH electrocatalyst by galvanic replacement toward ethanol oxidation in alkaline media. *Ultrasonics Sonochemistry*, 51, 478-486.
35. Maitya, S., Harisha, S., Eswaramoorthy, M. (2019). Controlled galvanic replacement of Ni in Ni(OH)₂ by Pd: A method to quantify metallic Ni and to synthesize bimetallic catalysts for methanol oxidation. *Materials Chemistry and Physics*, 221, 377-381.
36. Van Vinh, P., Ta, V. (2017). Synthesis of NiPt alloy nanoparticles by galvanic replacement method for direct ethanol fuel cell. *Hydrogen energy*, 42, 13192-13197.
37. Hu, S., Ribeiro, E., Tian, M., Mukherjee, D. (2016). Tandem laser ablation synthesis in solution-galvanic replacement reaction (LASIS-GRR) for the production of PtCo nanoalloys as oxygen reduction electrocatalysts. *Journal of Power Sources*, 306, 413-423.
38. Hu, S., Goenaga, G., Melton, C., Zawodzinski, T. (2016). PtCo/CoO_x Nanocomposites: Bifunctional Electrocatalysts for Oxygen Reduction and Evolution Reactions Synthesized via Tandem Laser Ablation Synthesis in Solution-Galvanic Replacement Reactions. *Catalysis B: Environmental*, 182, 286-296.
39. Hsu, C., Huang, C., Hao, Y., Liu, F. (2012). Au/Pd core-shell nanoparticles for enhanced electrocatalytic activity and durability. *Electrochemistry Communications*, 23, 133–136.
40. Kuntiyi, O., Shepida, M., Sus, L., Zozulya, G., Korniy, S. (2018). Modification of silicon surface with silver, gold and palladium nanostructures via galvanic substitution in DMSO and DMF solutions. *Chemistry & Chemical Technology*, 12, 305–309.
41. Dobrovets'ka, O., Kuntiyi, O., Zozulya, G., Saldan, I., Reshetnyak, O. (2015). Galvanic deposition of gold and palladium on magnesium by the method of substitution. *Materials Science*, 51, 418–423.
42. Kuntiyi, O., Zozulya, G., Shepida, M., Nichkalo, S. (2019). Deposition of nanostructured metals on the surface of silicon by galvanic replacement: a mini-review. *Voprosy khimii i khimicheskoi tekhnologii*, 124(3), 74–82.
43. Lahiri, A., Pulletikurthi, G., Endres, F. (2019). A Review on the Electroless Deposition of Functional Materials in Ionic Liquids for Batteries and Catalysis. *Frontiers in Chemistry*, 7, 13.

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ОДЕРЖАННЯ МЕТАЛЕВОЇ ЕЛЕКТРОКАТАЛІТИЧНОЇ НАНОСТРУКТУРОВАНОЇ ПОВЕРХНІ МЕТОДОМ ГАЛЬВАНІЧНОГО ЗАМІЩЕННЯ (ОГЛЯД)

Розкрито можливості методу гальванічного заміщення в формуванні металевої наноструктурованої поверхні для електрокаталітичних процесів. Ґрунтуючись на електрохімічному механізмі процесу та враховуючи тип підкладки, наведено такі напрями застосування цього методу: синтез металевих наноструктур та модифікація поверхні металів. Серед успіхів у напрямі модифікації поверхні продемонстровано ефективність осадження наноструктурних металів гальванічним заміщенням у середовищі органічних апротонних розчинників та іонних рідин. Відзначено роль середовища у керованому формуванні геометрії наночастинок металевого осаду.

Ключові слова: електрокаталізатори, гальванічне заміщення, металеві наноструктури, модифікація поверхні.