UDC 621.35

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NANOSCALE GALVANIC REPLACEMENT IN NON-AQUEOUS MEDIA: A MINI-REVIEW

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This mini-review summarizes the publications of the last decade dedicated to the study of the formation of metal nanostructures by galvanic replacement reaction in a non-aqueous medium (organic solvents and ionic liquids). It is shown that among modern methods of surface modification of nanostructures, galvanic replacement reaction belongs to one of the most effective ones in terms of preparing new materials and application of metal films. However, controlled formation of nanostructures is not always possible in aqueous solutions due to the occurrence of side chemical and electrochemical processes. The latter can be prevented in non-aqueous media, making them promising in chemistry of nanomaterials. A significant difference between the formation of M_1/M_2 nanostructures, where either electronegative (Mg, Al, Si, Zn, Co) or electropositive (Cu, Ag) elements serve as a sacrificial surface (M_1), is illustrated by the galvanic replacement reactions occurring in organic solvents (ethanol and organic aprotic solvents) and ionic liquids. The data on the influence of the nature of non-aqueous media and the basic parameters of the galvanic replacement process (solution composition, temperature and duration) on the deposits morphology and the geometry of the deposited particles are reported. It is shown that the galvanic replacement method in a non-aqueous medium promotes the controlled deposition of metallic nanoparticles on the macro- and nanosurfaces of the substrate and allows obtaining nanomaterials with predetermined functional properties.

Keywords: galvanic replacement, organic solvents, ionic liquids, metal nanoparticles, nanostructures.
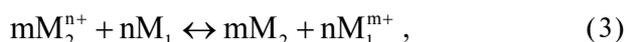
Introduction

Nanoscale galvanic replacement (NGR) is one of the promising areas of chemical nanomaterials, that has been developing rapidly in the last decade [1−11]. This is due to relative simplicity of the practical implementation of the galvanic replacement and their ample capabilities to yield functional nanostructured materials on metal [1,2,4] and semiconductor [6,10] surfaces. There are two following main types of NGR: (1) deposition of nanoparticles on macro-surfaces [1,6−10,12,13], and (2) fabrication of metal nanostructures [2−5,11,14,15], preferably mono-, bimetal (core@shell, hollow) and framework nanoparticles. The morphology of these deposits and the geometry of the nanostructures are determined by thermodynamic and kinetic parameters, which are interdependent and change in the course of galvanic replacement reactions. The galvanic replacement reactions are spontaneous, which complicates the controlled formation of metal nanostructures with specified characteristics.

Galvanic replacement reactions occur via an electrochemical mechanism and include two main electrode reactions: the dissolution of the sacrificial anode surface M_1 (1) and the cathodic reduction of deposited metal ions M_2^{n+} (2). Moreover, the galvanic replacement, which can be represented by the total reaction (3), is a spontaneous, multifactorial and reversible process. Its rate and, accordingly, the conditions of the formation of a metal deposit on the surface of the sacrificial substrate depend first on the value of the electromotive force (ΔE). The latter is influenced by the nature of M_1 and M_2 (4), the concentration of ions of the recovered metal M_2^{n+} and the temperature. Therefore, these three factors are fundamental in the processes of nucleation and growth of nanoparticles, which determines their

geometry and morphology of deposit.

$$M_1 \rightarrow M_1^{m+} + me , \quad (1)$$

$$M_2^{n+} + ne \rightarrow M_2 , \quad (2)$$

$$mM_2^{n+} + nM_1 \leftrightarrow mM_2 + nM_1^{m+} , \quad (3)$$

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

In aqueous solutions commonly used in NGR, the passage of side electrochemical processes is possible together with the main electrode reactions (1) and (2). For example, these can be electroreduction of hydrogen at the cathode surfaces, electrochemical corrosion of the substrate at the M_1/M_2 contact points, passivation of the substrate surface, and the like. This creates additional difficulties in the controlled formation of nanoparticle geometry and deposit morphology. The non-aqueous media, in particular organic solvents and ionic liquids (IL), allow eliminating these drawbacks of aqueous solutions, which expands opportunities of performing galvanic replacement reactions to produce new nanomaterials.

Galvanic replacement in organic solvents

Both protic polar organic solvents (ethanol and, ethylene glycol) and aprotic (DMSO, DMF and AN) ones can be used as a medium, which is indifferent to M_1 and M_2. This enables NGR to be carried out without by-processes on electrochemically active sacrificial macro-surfaces and nanoparticles (Table 1). Such solvents also minimize the number of precursors, in particular buffer additives, since there is no hydrolysis of ions. Molecules of high-donor aprotic solvents form stable solvates with many cations of d-metals, and surface complexes with metal nanoclusters (MNCs) and nanoparticles (MNPs). This causes cathodic polarization and accordingly promotes the formation of nanosized particles.

The formation of a metal deposit during galvanic replacement occurs by the following basic

Table 1

**Conditions of nanoscale galvanic replacement in organic solvents**

Substrate	Metal	The composition of the solution	Temperature, ^0C	Process duration	MNPs size, nm	Ref.
Mg-disk	Pd	0.01 M PdCl$_2$ in DMF	60	1; 5; 10 min	Mg/AuNPs(50; 50; 200)	[12]
	Au	4 mM H[AuCl$_4$] in DMF	60	8 min	Mg/AuNPs~200	[13]
	Au–Pd	4 mM H[AuCl$_4$]+4mM PdCl$_2$	60	8 min	Mg/(Au–Pd)NPs<200	[13]
Mg-powder	Pd	0.01 M PdCl$_2$ in DMF	50	5 min	thorns, $\varnothing$<100	[12]
MgNPs (~85 nm)	Ag	0.5 mM AgNO$_3$ in EtOH	30	5 min	Mg/Ag nano-heterostructures, 3–30	[14]
MgNPs 200–300 nm	Au; Ag; Pd; Fe	K[AuCl$_4$]; AgNO$_3$; FeCl$_3$; Na$_2$[PdCl$_4$] in anhydrous EtOH	20	16 h	bimetallic architectures Mg/(Au; Ag; Pd and Fe)NPs	[15]
Si-plate	Au	2–8 mM H[AuCl$_4$] in DMSO	40–60	0.5–4	20–200	[16]
	Pd	(1–4) mM Pd(NO$_3$)$_2$ in DMSO	30–50	30–90 s	30–140	[17]
AgNPs, $\varnothing$=11 and 14 nm	Au	0.5 mM H[AuCl$_4$] in CHCl$_3$+oleylamine	50	–	Au/Ag alloy hollow structures $\varnothing$=~12; and ~15	[18]
AgNPs	Au	H[AuCl$_4$] in toluene+oleylamine	20	10 min	Au–Ag hollow nanostructures	[19]
AgNPs, <20 nm	Au	0.2 mM AuCl$_3$ in oleylamine+ +ortho-dichlorobenzene	60	15 min	Au–Ag hollow and alloy nanostructures	[20]
AgNPs, ~43 and ~53 nm	Au	5 mM H[AuCl$_4$] in toluene+oleylamine	60	–	Au–Ag nanoshells	[21]
AgNPs, ~25 nm	Au	AuCl$_3$ in MeOH; EtOH; DMF:toluene	65	2 h	Au–Ag hollow and semihollow alloyed NPs	[22]
Co particles, $\varnothing$~1 μm	Au	5 mM H[AuCl$_4$] in EG	20	60 min	hollow microsphere Co/AuNPs (40–100)	[23]
AgNPs, 17.5±5.4 nm	Au	5 mM H[AuCl$_4$] in CHCl$_3$+octadecylamine	20	–	hollow AuNPs<20 nm	[24]
Au–NiNPs	Au	H[AuCl$_4$]	70	3 h	AuNPs	[25]
Microrods CuTCNQ	Au	1 mM K[AuBr$_4$] in AN	20	4 h	CuTCNQ/Au nanocomposites	[26]
PtNi$_3$NPs	Sn	SnCl$_4$ in EG	20	30 min	(PtNiSn)NPs	[27]

O.I. Kuntyi, G.I. Zozulya, M.V. Shepida

mechanisms: Vollmer-Weber (island), Stranski-Krastanov (dendrite) or Frank-van der Merwe (layer) growth mode (Figure). First of all, they depend on the nature of the deposited metal M_2 and the sacrificial surface M_1, namely on their lattice crystal and the rate of the NGR process. If the lattice constants of M_1 and M_2 differ significantly, which complicates or even makes it impossible to mix their atoms with the formation of alloys, sediments of the recovered metal M_2 of an insular nature are formed (Figure, route A). Thus, the deposition of gold and silver on the magnesium surface (a=0.321, c=0.521 nm for Mg, a=0.408 nm for Au and a=0.409 nm for Ag) in aqueous solutions [14,28,29], ethanol [14,15] and dimethyl formamide [13] are subjected to the formation of island by the Vollmer-Weber mechanism. Due to the high rate of the electron-generating reaction (1) and low concentrations of the deposited metal ions M_2^{n+}, dendritic growth (i.e. Stranski-Krastanov mechanism) (Figure, route B) is possible. However, due to the significant difference of the lattice constants of M_1 and M_2, for example, silver can deposit on silicon [30] and aluminum [31], and gold can deposit on cobalt [23]. When the values of the parameters of the crystal lattices M_1 and M_2 are close (Cu; Ag; Au) and the rates of reactions (1) and (2) are low, formation of a layer of the recovered metal M_2 (Figure, route C) is widely used to obtain bimetallic systems, in particular core@shell and hollow nanoparticles [1,2,5,11,18−22,24].

A significant difference between organic solvent environments and aqueous solutions during galvanic replacement is mainly manifested in case of electronegative metals, which are characterized by high chemical activity (magnesium, aluminum and zinc). For example, galvanic replacement of silver and gold by magnesium nanoparticles in ethanol solutions of $AgNO_3$ or $H[AuCl_4]$ allows preparing nano-heterostructures with a given size and distribution of AgNPs or AuNPs on the surface of MgNPs [14,15]. This is essential to ensure their functional properties, in particular in catalysis and optoelectronics [14]. Heterostructures of Mg/M (M=Ag, Au and Pd) with a given content of metal deposit on the magnesium surface are also obtained in high-donor organic aprotic solvents [12,13]. The absence of adverse reactions allows depositing gold and silver films [28], which are formed by the growth of metal islands followed by their agglomeration; these films exhibit a good adhesion to the substrate. A non-aqueous medium is also effective for codeposition of metals with controlled content of components, as exemplified by the galvanic replacement of Au−Pd films on magnesium in DMF solutions [13].

In aqueous solutions, preparation of such deposits is complicated by a high electronegativity of magnesium $\left(E^0_{Mg^{2+}/Mg} = -2.36 \text{ V}\right)$ as a sacrificial metal. This involves a relatively high values of ΔE (4), causing a high rate of electron-generating reaction (1). Therefore, in addition to the basic metal recovery
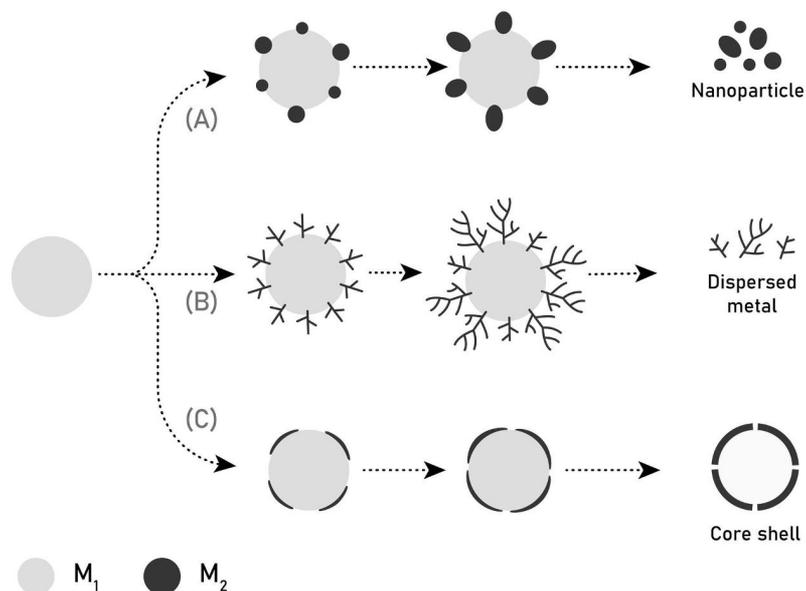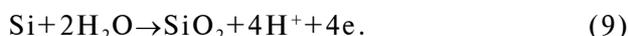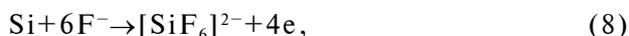

Scheme of formation of metal deposit during galvanic replacement reactions via the following mechanisms:
A − Vollmer-Weber (island); B − Stranski-Krastanov (dendrite) growth mode in non-aqueous and aqueous solutions;
C − Frank-van der Merwe (layer)

reaction, adverse reactions (5) at pH≥7 and reactions (5) and (6) at pH<7 are observed in the cathode areas. This is due to the contact corrosion of a sacrificial metal. The sacrificial metal can be completely dissolved with the formation of nanoparticles or dispersed sediments of recoverable metals (Figure). Therefore, the galvanic replacement with the use of MgNPs in aqueous solutions of AgNO$_3$ or H[AuCl$_4$] produces AgNPs or AuNPs [13], whereas the use of magnesium powder yields dispersed gold [29].

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2, \qquad (5)$$

$$Mg + 2H^+ \rightarrow Mg^{2+} + H_2. \qquad (6)$$
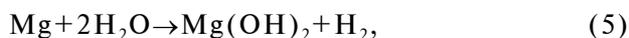
In aqueous solutions, the electron-generating process at the anode sites can also be accelerated due to adverse reactions. Thus, during the deposition of silver on a silicon surface in fluoride-containing solutions (7), a side reaction (9) occurs together with the main electron-generating reaction (8). This causes an increase in the rate of recovery at the cathode areas, resulting in the formation of dendritic silver [30]. The deposition of silver in DMF solutions does not lead to dendritic formation [32], apparently in the absence of reaction (9).

$$4Ag^+ + Si + 6F^- \rightarrow 4Ag + [SiF_6]^{2-}, \qquad (7)$$

$$Si + 6F^- \rightarrow [SiF_6]^{2-} + 4e, \qquad (8)$$

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e. \qquad (9)$$

The formation of metallic nanostructures is very sensitive to kinetic and thermodynamic factors [33], which complicates the implementation of nanoparticle design with controlled geometry, especially in aqueous solutions [1,2,5,11,30]. The following advantages of the organic solvent environment are mentioned in literature: (1) the possibility of using small nanoparticle templates and (2) the controlled formation of cavity and frame nanoclusters of a given composition. Thus, the indifference of organic solvents to MNPs makes it possible to use 14, 11 nm [18] and even <6 nm [20] nanoparticles as templates. Refs. [18,19] demonstrated the effectiveness of a combination of organic solvent and surfactant (oleylamine) as a medium for the synthesis of well-controlled Au−Ag hollow nanostructures via the reaction between Ag nanocubes and H[AuCl$_4$].

Indifference of the organic medium to MNPs also allows using elevated temperatures to form solid alloys of sacrificial and deposited metals. Thus, the galvanic replacement of AgNPs+H[AuCl$_4$] in the toluene-oleylamine system at 60^{0}C makes it possible to obtain cavity nanostructures of an Ag−Au alloy of controlled composition [20]. Together with the change in temperature, different organic solvents, such as methanol, ethanol and dimethyl formamide-toluene, can be used to adjust the rate of the galvanic replacement process [22]. This allows controllable delivering hollow and non-hollow Ag−Au alloy nanoparticles with predetermined content of components.

A comparative analysis of the synthesis of hollow AuNPs and PtNPs was conducted by means of galvanic replacement in aqueous solution and chloroform, respectively [22]. It was shown that the hollow NPs synthesized in the non-aqueous medium differed by the more compact and uniform Au and Pt shells.

The addition of surfactant of different nature to organic solvents can significantly influence the direction of the galvanic replacement process. Thus, only the deposition of gold (reaction (10)) occurs in toluene solution of H[AuCl$_4$] containing oleylamine. In the presence of didodecyldimethylammonium bromide, in addition to the galvanic replacement, gold can partially dissolve in the most active sites (protrusions) according to the reaction (11), altering the morphology of deposits [24]. Therefore, the addition of some surfactant and change of the ionic composition of the solution may cause certain transformation of the nanostructures.

$$2[AuCl_4]^- + 3Ni \rightarrow 2Au + 3Ni^{2+} + 8Cl^-, \qquad (10)$$

$$[AuBr_4]^- + 2Au \rightarrow 3AuBr + Br^-. \qquad (11)$$
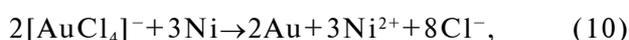
The organic solvent environment seems to be promising to synthesize multimetallic nanoparticles. The preparation of triple PtNiSn nanowires by galvanic replacement on the surface of PtNi$_3$ nanoparticles according to reaction (12) in ethylene glycol was demonstrated [24]. In this case, the hydrolysis of SnCl$_4$ is decelerated even at elevated temperatures, which promotes the formation of the Pt−Ni alloy.

$$2Ni(PtNi_3) + SnCl_4 \rightarrow 2NiCl_2 + PtNiSn. \qquad (12)$$

Galvanic replacement in ionic liquids

Ionic liquids (ILs), unlike to organic solvents, consist only of ions. Therefore, ILs are characterized by relatively high conductivity [7,34,35], which allows using them as effective media for electrodeposition

O.I. Kuntyi, G.I. Zozulya, M.V. Shepida

of metal coatings [36] as well as deposition of metals and synthesis of nanostructures by galvanic replacement method (Table 2). A separate group of ionic liquids are the so-called deep eutectic solvents (DESs) (or low-temperature eutectic solvents), which have some advantages over ionic liquid, in particular they are more resistant to moisture and air, have higher viscosity and are cheaper [51].

In addition, anions in ionic liquids form complexes with cations of deposited metals. Since in such an environment it is possible to change the ionic composition via changing the nature of an

Table 2

Conditions of nanoscale galvanic replacement in ionic liquids*

Substrate	Metal	The composition of the solution	Temperature, ^{0}C	Process duration	MNPs size, nm	Ref.
Mg	Cu	0.1 M CuCl in BMP–DCA IL	20	24 h	CuNPs agglomerated spherical clusters, $\varnothing$=~100	[37]
	Ni	0.1 M NiCl$_2$ in BMP–DCA IL			NiNPs film consists <3	
	Zn	0.1 ZnCl$_2$ in BMP–DCA IL			ZnNPs nano-whiskers<50	
	Ti	0.1 TiF$_4$ in BMP–DCA IL			loose deposits	
Mg, Al$_2$Mg$_3$	Al	AlCl$_3$+[EMIM]Cl or [Al$_2$Cl$_7$]$^-$+[EMIM]	20	–	Al Nanoporous ~200	[38]
Al$_2$Mg$_3$	Al	AlCl$_3$ in [EMIM]Cl	20	8 h	Al nanoporous films	[39]
Al	Ni	0.15 M NiCl$_2$ in ChCl–EG DES	50	60, 20, 1000, 1800 s, 4 h	Ni layer with spherical particles	[40]
Al	Cu	0.15 M CuCl$_2$ in 1M ChCl:2EG+0.15 M thiourea	20	$1.0 \cdot 10^2$, $7.2 \cdot 10^2$, $3.6 \cdot 10^3$, $1.44 \cdot 10^4$ s	–	[41]
Si	Sb	0.1 M SbCl$_3$ in [Py$_{1,4}$]TFSA	20	10 min	morphology is seen	[10]
	Ag	0.1 M AgTFSA			porous network-like structure	
Zn	Ni	0.05 M NiCl$_2$ in [BMP][TFSA]	50, 80	15, 30, 60 min	porous and hollow Ni	[42]
GaNPs, $\varnothing$=40–70 nm	Sb	0.1 M SbCl$_3$–[Py$_{1,4}$]TFSA, 25 mM SbCl$_3$–[Py$_{1,4}$]TFSA	20	2, 3, 6, 24, 48 min	Ga/Sb, 30–200	[43]
Ni	Au	5 mM (AuCl, AuCN, KAu(CN)$_2$) in Ethaline 200	80	40 min	Au coatings	[44]
Cu	Ni	0.10 M NiCl$_2$ in ethaline (1 (ChCl):2 (EG))	80	5, 10, 30 min, 1, 5, 12, 24 h	NiNPs 89.6±3.5	[45]
Cu	Ag	10 mM AgCl in 1ChCl:2EG	20	5 min	Ag ~500	[46]
Cu	Ag	0.01 M AgCl in 1ChCl:2EG 0.1 M AgCl in 1ChCl:2EG	20, 50	1, 5, 10 min	nanoporous network of Ag films with ligament and channel width in the range of 20–80	[47]
Cu nanowires	Ag	1 mM Ag salt in [P$_{1,4}$NTF$_2$]	20	1–30 min	Cu@Ag core–shell nanowires	[48]
AgNPs, $\varnothing$=15–20 nm	Au–Ag	K[AuBr$_4$] in [BMIM][BF$_4$]	20	48 h	Au–Ag dendritic nanostructures (10–100)	[49]
AgNPs	Au–Ag	1 mM [AuBr$_4$]$^?$ in BMIM][BF$_4$]	20	–	Au–Ag alloyNPs	[50]

Note: * − BMP−DCA IL − butylmethylpyrrolidinium−dicyanamide ionic liquid; [EMIM] − 1-ethyl-3-methyl imidazolium; ChCl−EG − choline chloride-ethylene glycol (ethaline); [Py$_{1,4}$]TFSA − 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide; [BMP][TFSA] − butylmethylpyrrolidinium bis(trifluoromethylsulfonyl)amide; [P$_{1,4}$NTF$_2$] − 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide; [BMIM][BF$_4$] − 1-butyl-3-ethylimidazolium tetrafluoroborate.

anion, it is consequently possible to influence the composition of the complexes and, most importantly, the value of the standard redox potentials of metals. This makes it possible to carry out such galvanic replacement reactions that cannot be performed in aqueous solutions and organic solvent media. Thus, the standard potentials of nickel and copper in deep eutectic solvent ethaline are changed due to complexation with DES ions and stabilization of Cu(I) and the following inequality becomes valid: $E^0_{Ni^{2+}/Ni} > E^0_{Cu^+/Cu}$ (-0.154 V and -0.350 V, respectively). This allows depositing nickel on the copper surface according to reaction (13) [45]. In aqueous or organic solvent-based solutions of simple salts $\left(E^0_{Cu^{2+}/Cu} = 0.34\text{ V},\ E^0_{Ni^{2+}/Ni} = -0.257\text{ V}\right)$ quite the contrary copper deposits on a nickel surface.

$$2Cu(s)+Ni(II)\ (\text{in DES})\rightarrow$$
$$\rightarrow Ni(s)+2Cu(I)\ (\text{in DES}). \qquad (13)$$
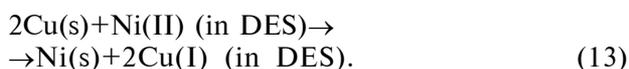
The special features of ionic liquids, such as the prevention of by-processes and the control of the reaction rate via adjusting complexation and viscosity) appreciably affect the formation of nanostructures by galvanic replacement technique. This makes it possible to provide almost complete reproduction (cloning) of the geometry of the sacrificial nanoscale. Therefore, galvanic replacement in the ILs can be widely used to deposit metal coatings [37,40,41,44,46,47] and obtain metal nanostructures [38,39,42,43,45,48-50].
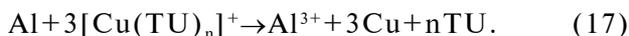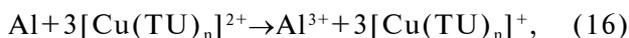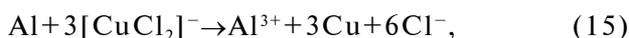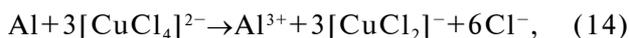
Deposition of metal coatings

Unlike aqueous solutions, galvanic replacement on the surface of active metals (magnesium, aluminum and their alloys) in ionic liquids yields nanostructured copper and nickel films [37,40,41]. They are used as separate functional coatings (copper and zinc) and a sublayer for electrochemical nickel plating.

The deposition of Cu, Ni, Zn and Ti can be carried out in butylmethylpyrrolidinium−dicyanamide (BMP−DCA) IL. ILs with DCA-anions are water- and air-stable electrolytes with low viscosity and high conductivity [37]. Another reason for choosing DCA is its high solubility with respect to metal salt precursors. BMP$^+$ was chosen as a cation because its cathodic stability limit (associated with the BMP$^+$ reduction) is beyond the redox potential of Mg. In ionic liquids, as compared with aqueous solutions, copper is deposited only from stable Cu(I) complexes, for example, $[Cu(DCA)_2]^-$ [37], $[CuCl_2]^-$, $[Cu(TU)_n]^+$ [41]. This provides deposition of nanostructured copper coatings with a particle size of ~100 nm [37]. Nickel and zinc coatings are also

nanostructured [37].

The deposition of nanostructured copper on the aluminum surface by galvanic replacement in aqueous solutions was performed in strongly alkaline solutions or solutions containing fluoride ions to remove the oxide film [31]. The use of an ILs environment prevents the formation of the oxide film, so there is no need in etching additives for the deposition of metals on aluminum [40,41]. Ionic liquids, as noted above, stabilize the oxidation state ($+1$) to form strong complexes with Cu(I). Thus, in ChCl-ethylene glycol (ChCl−EG), the galvanic replacement occurs stepwise, where $[CuCl_2]^-$ is initially formed by the reduction of Cu(II) aluminum to Cu(I) (reaction (14)). Subsequently, galvanic replacement occurs (reaction (15)), where nanostructured film deposits are formed as a result of a higher stability of the $[CuCl_2]^-$ ions as compared with $[CuCl_4]^{2-}$. An analogy is also observed in the formation of a stable complex $[Cu(TU)_n]^+$ by reaction (16), which promotes nanostructured film deposition by reaction (17) [41].

$$Al+3[CuCl_4]^{2-}\rightarrow Al^{3+}+3[CuCl_2]^-+6Cl^-, \quad (14)$$

$$Al+3[CuCl_2]^-\rightarrow Al^{3+}+3Cu+6Cl^-, \qquad (15)$$

$$Al+3[Cu(TU)_n]^{2+}\rightarrow Al^{3+}+3[Cu(TU)_n]^+, \quad (16)$$

$$Al+3[Cu(TU)_n]^+\rightarrow Al^{3+}+3Cu+nTU. \qquad (17)$$

The formation of stable Ag(I) complexes with ionic liquids components contributes to the formation of nanostructured silver films on the copper surface by galvanic replacement [46,47]. However, the control of deposits morphology (size of silver grains and nanopores) is ensured by the adjustment of basic parameters of NGR: concentration of Ag(I) complexes, process duration and temperature [47].

### Synthesis of metal nanostructures

The formation of Ni-hollow tubes from Zn in nanoparticles [BMP][TFSA] can be considered as an example of the efficiency of an ionic fluid environment to produce nanostructures by NGR [42]. The presence of the complex $[NiCl_4]^{2-}$ due to the interaction of $NiCl_2$ and [BMP][Cl] and high viscosity provide the required rate of the GR process to reproduce the template structure.

Galvanic replacement in ionic liquids is also effective for the synthesis of semiconductor nanostructures [10,43]. Thus, GaSb is directly synthesized at room temperature from a solution of $SbCl_3$/IL on electrodeposited Ga. Moreover, the content of the components in the binary system and

O.I. Kuntyi, G.I. Zozulya, M.V. Shepida

its structure regulate the composition of the ionic liquid [43].

The features of modification of the silicon surface by metal nanoparticles via galvanic replacements in ionic liquids differ significantly from those typical of aqueous solutions. In aqueous solutions, HF is a mandatory component of the solution [6, 30] for binding Si(IV) to form complex (8) and dissolve passive SiO_2 film (9). ILs prevent the formation of SiO_2, hence the process (7) can be performed without the use of HF. 1-Butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide ([Py1,4] TFSA was used to deposit Sb and Ag on the silicon surface with the formation of $[Ag(TFSA)_3]^{2-}$ and $[SbCl_2(TFSA)_2]^-$ [10].

One of the new and promising directions for the use of galvanic replacement in ionic liquids is the formation of nanoporous surfaces of active metals. Thus, using the system $[EMIM]^+$ $[Al_2Cl_7]^-$, nanoporous aluminum was prepared for the first time [38,39], which is impossible in aqueous solutions. NGR proceeds without adverse processes according to reaction (18), where pure Mg or magnesium in the Al_2Mg_3 alloy are sacrificial materials [38,39].

$$3Mg(Al_2Mg_3)+8[Al_2Cl_7]^-\rightarrow$$
$$\rightarrow Al+3Mg^{2+}+14[AlCl_4]^-. \qquad (18)$$
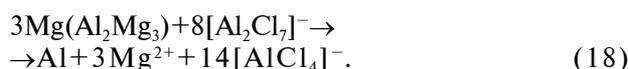
The peculiarity of NGR on the Al_2Mg_3 alloy is that two processes occur simultaneously: (1) the formation of a nanoporous skeleton of aluminum due to the dissolution of magnesium, and (2) the deposition of aluminum. This results in the formation of durable and crack-free aluminum with 3D nanoporous structure and a wide range of functional properties.

Conclusions

Among the up-to-date methods of surface modification by nanostructures, galvanic replacement is one of the most effective in terms of preparing new materials and depositing metal films. In a non-aqueous medium organic solvents and ionic liquids, the galvanic replacement method contributes to the controlled deposition of metal nanoparticles on the macro- and nanosurfaces of the substrate and allows obtaining nanomaterials with specified functional properties.

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НАНОРОЗМІРНЕ ГАЛЬВАНІЧНЕ ЗАМІЩЕННЯ У НЕВОДНИХ СЕРЕДОВИЩАХ: МІНІ-ОГЛЯД

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У міні-огляді проаналізовано публікації останнього десятиліття, присвячені дослідженню процесу формування металевих наноструктур методом гальванічного заміщення у неводному середовищі − органічних розчинниках та іонних рідинах. Показано, що серед сучасних способів модифікації поверхні наноструктурами метод гальванічного заміщення відносять до одного з найбільш ефективних в аспекті одержання нових матеріалів і нанесення металевих плівок. Проте у водних розчинах не завжди можливе контрольоване формування наноструктур з причини перебігу побічних хімічних й електрохімічних процесів. Останні нівелюються неводними середовищами, що робить їх перспективними у хімії наноматеріалів. Суттєву відмінність формування наноструктур M_1/M_2, де жертовною поверхнею (M_1) є або електронегативні (Mg, Al, Si, Zn, Co), або електропозитивні (Cu, Ag) елементи, проілюстровано на прикладі гальванічного заміщення в органічних розчинниках (етанолі, органічних апротонних розчинниках) та іонних рідинах. Наведено дані про закономірності впливу природи неводного середовища й основних параметрів процесу гальванічного заміщення (складу розчину, температури, тривалості) на морфологію осаду та геометрію осаджених частинок. Показано, що метод гальванічного заміщення у неводному середовищі сприяє контрольованому осадженню металевих наночастинок на макро- та наноповерхню підкладки з одержанням наноматеріалів із заданими функціональними властивостями.

Ключові слова: гальванічне заміщення, органічні розчинники, іонні рідини, металеві наночастинки, наноструктури.

NANOSCALE GALVANIC REPLACEMENT IN NON-AQUEOUS MEDIA: A MINI-REVIEW

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This mini-review summarizes the publications of the last decade dedicated to the study of the formation of metal nanostructures by galvanic replacement reaction in a non-aqueous medium (organic solvents and ionic liquids). It is shown that among modern methods of surface modification of nanostructures, galvanic replacement reaction belongs to one of the most effective ones in terms of preparing new materials and application of metal films. However, controlled formation of nanostructures is not always possible in aqueous solutions due to the occurrence of side chemical and electrochemical processes. The latter can be prevented in non-aqueous media, making them promising in chemistry of nanomaterials. A significant difference between the formation of M_1/M_2 nanostructures, where either electronegative (Mg, Al, Si, Zn, Co) or electropositive (Cu, Ag) elements serve as a sacrificial surface (M_1), is illustrated by the galvanic replacement reactions occurring in organic solvents (ethanol and organic aprotic solvents) and ionic liquids. The data on the influence of the nature of non-aqueous media and the basic parameters of the galvanic replacement process (solution composition, temperature and duration) on the deposits morphology and the geometry of the deposited particles are reported. It is shown that the galvanic replacement method in a non-aqueous medium promotes the controlled deposition of metallic nanoparticles on the macro- and nanosurfaces of the substrate and allows obtaining nanomaterials with predetermined functional properties.

Keywords: galvanic replacement; organic solvents; ionic liquids; metal nanoparticles; nanostructures.

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