G. I. Zozulia[1], M. V. Shepida[1], Ç. Güçlüten[2], O. I. Kuntyi[1]
[1] Lviv Polytechnic National University,
Department of Chemistry and Technology of Inorganic Substances
[2] Adana Alparslan Türkeş Science and Technology University, Turkey
halyna.i.zozulia@lpnu.ua

DECORATION OF 3D NICKEL AND COPPER SURFACES WITH METALLIC NANOPARTICLES AND NANOSTRUCTURES BY GALVANIC REPLACEMENT. MINIREVIEW

The effectiveness of the galvanic replacement method for decorating a porous surface with metal nanoparticles and nanostructures is considered. It is shown that depending on the functional purpose, foam, porous, and dendritic metal 3D substrates are mainly used for modification by galvanic replacement. In particular, these are nickel and copper substrates on which noble metals are deposited. The peculiarities of the formation of nanosized deposits on porous copper and nickel surfaces depending on the structure of the latter and the conditions of galvanic substitution are given. The main areas of their application are specified.

Key words: porous metals; foam; nanodendrite; galvanic replacement; metal nanoparticles; nanostructures; nickel and copper surfaces.

Introduction

In the last decade, porous metal surfaces have attracted the attention of researchers, primarily due to the peculiarities of their structure and large specific surface area [1–6]. This determines their unique functional properties and, accordingly, wide areas of use, in particular, catalysis and energy storage. The active surface area of porous metals is especially effective for electrochemical applications. For the latter, in addition to the specific surface area, an important role is played by the penetration of liquids into the pores. Moreover, the geometry of the latter significantly affects the diffusion processes in porous electrodes. Thus, with a decrease in pore size from micron to submicron-nano-sized and nano-sized pores, the BET surface area increased up from 2 to 17 and 101 $m^2 \cdot g^{-1}$, respectively [7]. However, with an increase in the specific surface area, the permeability of liquids into pores gets more complicated, and it is especially low in nanoporous metals. So, there is a collision between pore sizes and mass transport. One of the ways to solve this problem is to decorate the porous surface with metal nanoparticles (MNPs) and nanostructures [8–13]. The most studied are pore modification by electrochemical deposition and galvanic replacement. Moreover, the latter method has advantages over electrodeposition, namely as follows. The uniformity of metal deposition on the relief surface of the substrate is much better. The process does not require an external supply of electric current, which makes it possible to decorate porous substrates of various geometries, which is important in the technological aspect.

Galvanic replacement proceeds according to the total reaction (1), the electromotive force (DE) of which is identical to the rate of the process and depends on the difference in the values of the electrode potentials of the deposited (M_1) and sacrificial (M_2) metals: $DE = E_{M_1^{n+}/M_1} - E_{M_2^{m+}/M_2}$. The shape and size of the particles of the deposited metal also depend on the value of DE – the larger it is, the smaller the particles are, up to nano-sized ones [14–17]

$$mM_1^{n+} + nM_2 \rightleftharpoons mM_1 + nM_2^{m+}, \quad (1)$$
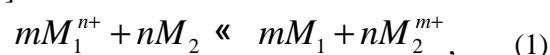
Galvanic replacement makes it possible to decorate the porous surface in stages by depositing one, two or more metals (Fig. 1). This makes it possible to form bi-, tri- and polymetallic structures that are effective in catalysis.

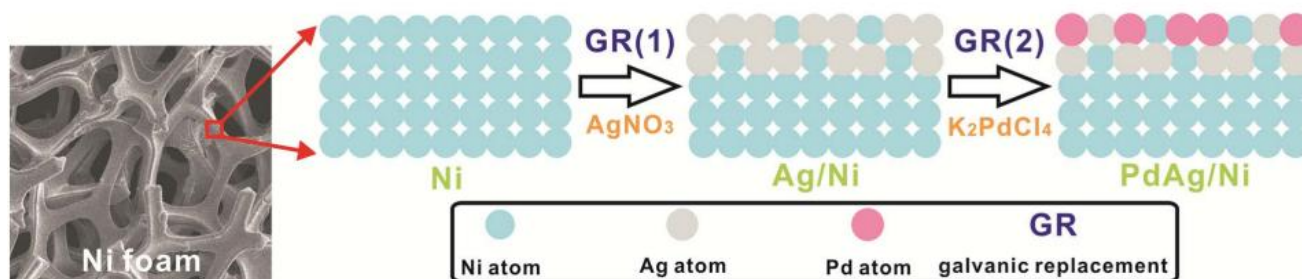G. I. Zozulia, M. V. Shepida, Ç. Güçlüten, O. I. Kuntyi

Fig. 1. Illustration of the preparation process of PdAg/Ni foam electrocatalysts [18]

Depending on the functional purpose, the following metal 3D substrates are preferably used for decorating with nanoparticles and nanostructures by galvanic replacement: foam, porous, and dendritic. In most cases, these are nickel and copper substrates on which noble metals are deposited. The values of the standard electrode potentials of the specified sacrificial metals (($E^0_{Ni^{2+}/Ni} = -0.25$ V; $E^0_{Cu^{2+}/Cu} = 0.34$ V) are significantly lower than the E^0 values of the deposited metals ($E^0_{Ag^+/Ni} = 0.799$ V; $E^0_{Pd^{2+}/Pd} = 0.987$ V). So, the rate of the electrogenerating reaction (2) at the anode areas provides the conditions for the formation of nanostructures for reaction (3) at the cathode areas.

$$nM_2 \circledR nM_2^{m+} + me,$$ (2)

$$mM_1^{n+} + ne \circledR mM_1.$$ (3)
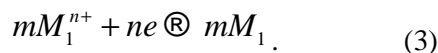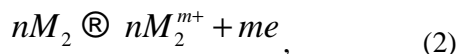
The aim of the work is a critical analysis of the scientific literature on the decoration of 3D nickel and copper substrates by the galvanic replacement method with nanoparticles and nanostructures of noble metals.

1. Sedimentation of nanosized metal particles on 3D nickel substrates

As a 3D nickel substrate, nickel foam is most often used [18–22], and electrochemically formed porous and dendritic deposits are less common [12]. In addition to copper, such surfaces are decorated only with noble metals – Ag, Pd, PtAu. Nanosized particles can be deposited in solutions of hydrated and complex ions of reducible metals on the surface of a 3D nickel substrate at millimolar concentrations of a metal precursor (Table 1). Galvanic replacement makes it possible to decorate the entire area of the nickel foam carcass, but the distribution of deposited nanoparticles is not uniform. The density of filling

on flat fragments of the carcass is much lower compared to filling on the rib's surface (Fig. 2). This is caused, first of all, by the higher surface energy of the latter, which is a factor of acceleration of the electron-generating reaction (2). As a result, the rate of metal recovery by reaction (3) is increased.
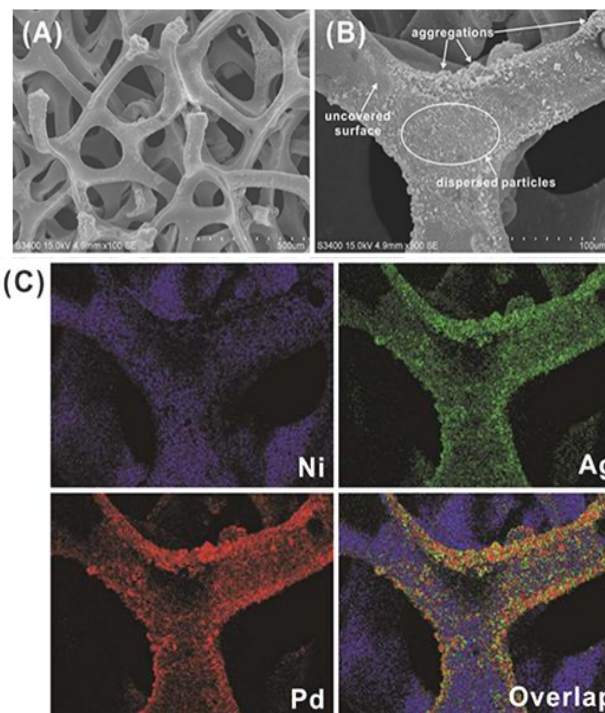

Fig. 2. SEM (A: ×100 times; B: ×500 times) and elemental mapping (C) images of the synthesized $Pd_{55}Ag_{45}/Ni$ foam [18]

Due to the large difference in the standard electrode potentials between the deposited metal (for example, palladium) and the sacrificial metal (nickel), as well as the factor of increasing the rate of galvanic replacement on the edges of the nickel carcass, the conditions for the formation of nanodendrites are achieved (Fig. 3).

Table 1

**Ni/M – Conditions for decorating 3D nickel substrate by galvanic replacement,
the geometry of the deposited metals (M) and the use of Ni/M composites**

M	Main reagents	t, $^{\circ}$C	t	The geometry of the deposited metal	Use	Ref.
Cu	CuSO$_4$	20	75 min	nanofilm	for electrocatalytic activity towards glycerol oxidation reaction	[12]
Ag	1) AgNO$_3$; 2) [Ag(S$_2$O$_3$)$_2$]$^{3-}$; 3) [Ag(S$_2$O$_3$)$_2$]$^{3-}$ + PVP 4) [Ag(NCS)$_4$]$^{3-}$	25–45	1) 1–50 h 2) 5–30 min 3) 1–15 min 4) 5–30 min	Ni 3D substrates with typical particle sizes of Ag < 100 nm	Ag-modified Ni foam electrodes for reductive dechlorination of chloroacetanilide herbicide	[19]
	AgNO$_3$	20	10 min	Ni 3D substrates with Ag nanoparticles	ternary PdAg/Ni architecture for methanol catalytic electrooxidation	[18]
Pd	PdCl$_2$	20	40 min	spongy Pd-arrays on a Ni foam substrate	Pd2/NF-PMS is an effective anode for the catalytic oxidation of methanol	[20]
	PdCl$_2$ + HCl	20	60 min	porous Ni/Pd	catalytically active electrodes for ethanol oxidation	[21]
PtAu	Na[AuCl$_4$] + K$_2$[PtCl$_4$]	-	-	PtAu nano- or microstructures on the surface of Ni foam	PtAu-Ni electrocatalytic electrodes for glycerol oxidation	[22]
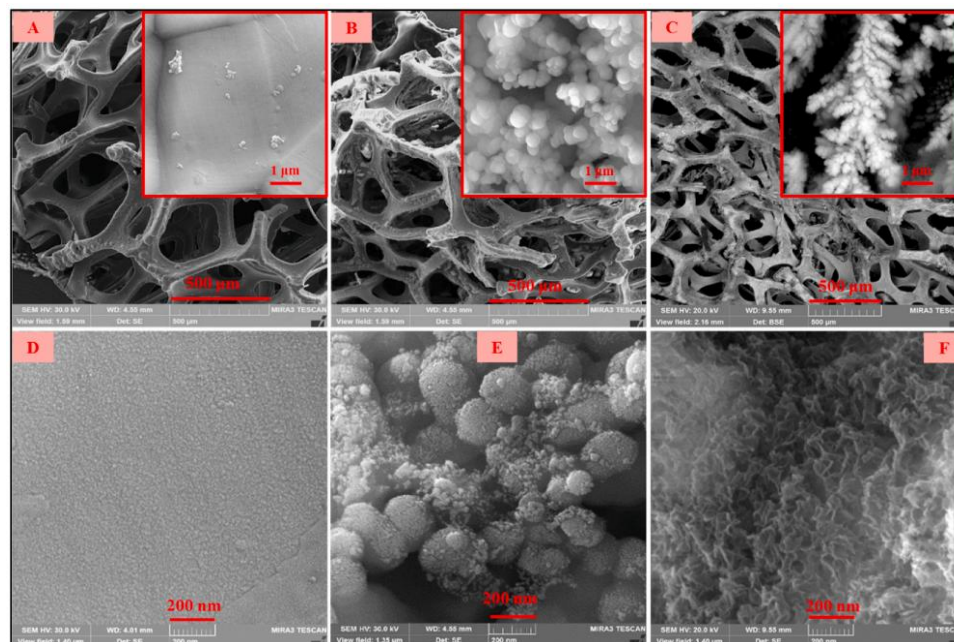
Fig. 3. Respectively, FESEM images of bare NF, NF-PMS, and Pd$_2$/NF-PMS in low (A, B, C) and high (D, E, F) magnification [20]

The high BET surface area of the sacrificial metal substrate is enhanced by the highly developed surface of the formed nanodeposit. This contributes to the synergism of the functional properties of such nanostructured materials. The high efficiency of the latter is confirmed by the nickel foam substrate decorated with palladium nanoparticles (Fig. 4).
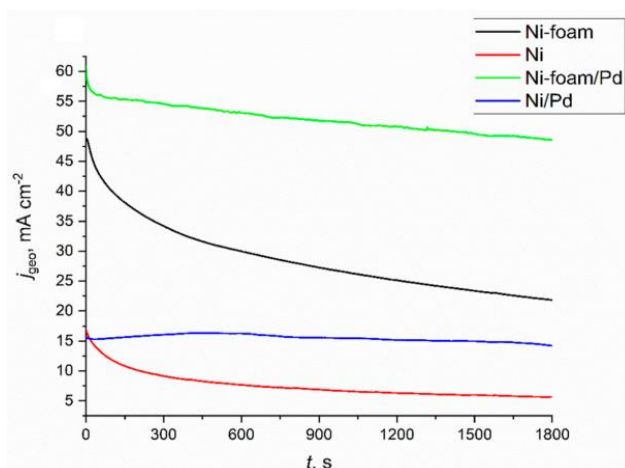
Fig. 4. Chronoamperometry in 1M NaOH + 1M ethanol addition for flat and porous Ni samples with and without the surface modification with Pd^{2+} ions. Modification time: 3600 s. E = 1.6 V [21]

In recent years, there has been increasing interest in the 3D substrate prepared by electrolysis in the mode of formation of porous and porous-dendritic deposit. Thus, work [12] showed that in electrolytes containing NH_4^+ ions, the value of the cathodic current density ($i_{cathode}$) has a controlled effect on the morphology of deposited nickel, in particular on the pore sizes and the geometry of nanodendrites. During electrolysis, the following two parallel reactions take place on the cathode: the electroreduction of nickel (4) and the formation of gaseous products – NH_3 and H_2 (5). With an increase in the $i_{cathode}$ value, the proportion of reaction (5) also increases. This leads to the formation of a more porous surface up to the formation of nanodendrites.

$$Ni^{2+} + 2e \circledR Ni, \qquad (4)$$
$$2 NH_4^+ + 2 e \circledR 2 NH_3 + H_2. \qquad (5)$$

2. Sedimentation of nanosized metal particles on 3D copper substrates

Almost all types of copper surfaces (foam, porous, dendritic) with a high specific area are used with 3D copper substrates, which are decorated with metal nanoparticles and nanostructure (Table 2). A feature of copper substrates is that the surface of this metal is catalytically active in many processes. Thus, for the electrochemical reduction of CO_2, copper cathodes are characterized by high efficiency [30]. In addition, the electrocatalytic activity in the conversion of carbon (IV) is also enhanced by CuO [25] and Cu_2O [27, 31, 32] on the copper cathode. So, the high efficiency of decorated 3D copper substrates is often the result of the synergistic action of copper and oxides and nanoparticles on its surface (Fig. 5).

Galvanic substitution on 3D copper substrates containing fixed CuO and Cu_2O on a metal conductor under conditions that ensure uniform distribution of oxide nanoparticles and deposited metal nanoparticles. An example of this implementation is the preparation of a modified Cu/CuO-Ag copper foam surface (Fig. 6). However, the issue of ensuring the uniform distribution of the specified decoration components to the depth of the 3D substrate, which is caused by the diffusion factor, is problematic and little studied.
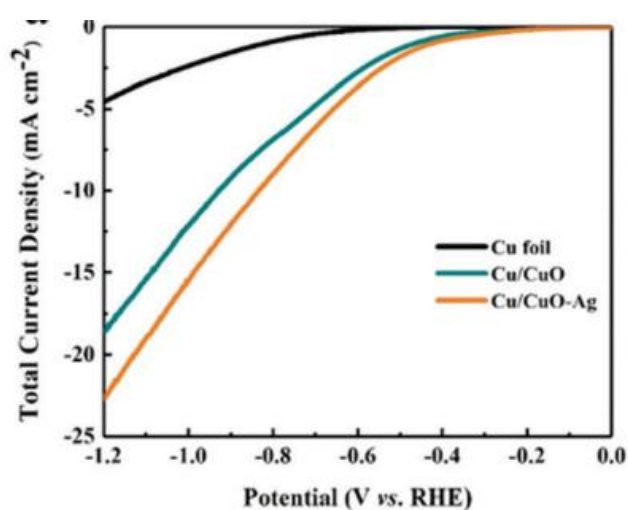
a
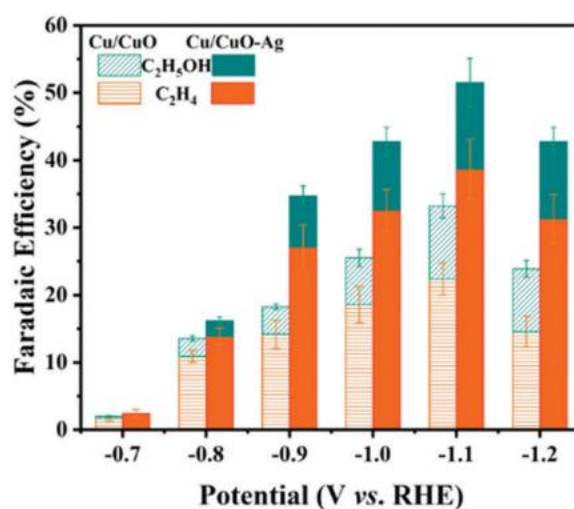
b

Fig. 5. Electrocatalytic carbon dioxide reduction performance on Cu/CuO, Cu/CuO-Ag and Cu foil catalysts [25]

Table 2

Conditions for decorating a 3D copper surface by galvanic replacement, the geometry of deposited metals (M) and the use of Cu/M nanomaterials

| M	Basic reagents	substrate	t, °C	t	The geometry of the deposited metal	Application	Ref.
Ag	AgNO$_3$	electrolytic copper nanodendrites	20	10; 20; 30 min	silver-plated copper nanodendrites	high electrocatalytic ability for H$_2$O$_2$ reduction, which was important for the design of a NaBH$_4$-H$_2$O$_2$ battery	[23]
	AgNO$_3$ + ПАР	copper nanodendrites	20	30 s	bimetallic Cu-Ag alloy on nanodendritic Cu nanostructures	photocatalytic efficiency for decolorization of azo dye avid violet 7	[24]
	AgNO$_3$	electrolytic copper foam	20	1; 3; 5 min	surface composition of Cu/CuO–Ag with a porous structure	to the design of efficient tandem catalysts for electrochemical CO$_2$ reduction	[25]
		porous copper	20	15–45 s	surface porous Cu/Ag composition with nanostructured silver	catalytically active cathodes for the electrochemical reduction of CO$_2$	[26]
Au	H[AuCl$_4$]	porous surface Cu/Cu$_2$O	22	1–5 min	Nanostructured Cu/Cu$_2$O/Au surface	for electrodes in electrochemical catalysis processes	[27]
		copper nanofabrics (Cu@Fabric)	20	1 h	Gold-decorated copper nanofabrics (Cu-Au$_x$@Fabrics)	effective for photocatalysis	[28]
PdPt	PdCl$_2$, PtCl$_4$ in solution HClO$_4$	copper foam	20	-	Binary nanosystem Pd$_{65}$Pt$_{35}$ (NFC)	stable nanofoam catalyst for electroreduction of hydrogen	[29]
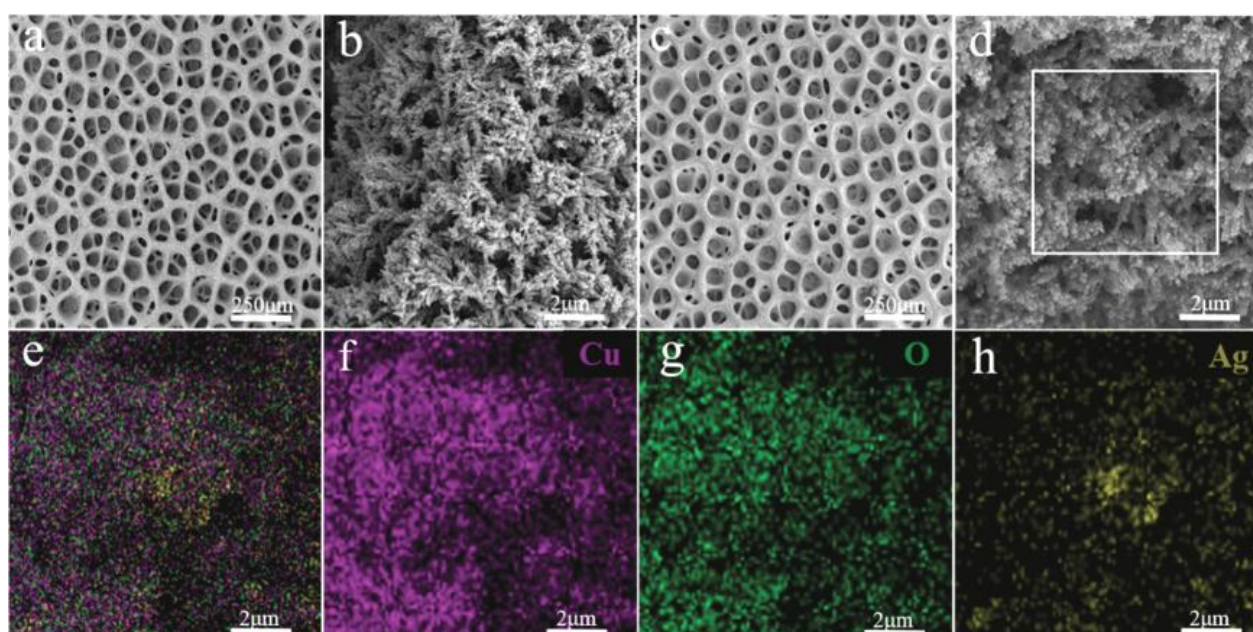
Fig. 6. SEM images (a) and (b) of Cu/CuO (c) and (d) SEM images of Cu/CuO-Ag (e–h) EDX images of overlap, Cu, O and Ag of Cu/CuO-Ag [25]

The galvanic substitution on the dendritic copper structure is little affected by the diffusion factor. Therefore, as a sacrificial substrate, you can use nanodendrites, characterized by a highly developed surface, a high specific area and a variety of geometries. The last factor contributes to the increase of catalytic centers. Therefore, decorated nanodendritic structures are often more effective than nanoparticle-decorated 2D surfaces. Evidence of this is the high catalytic activity of anodes based on dendritic Pd/Ag in electrocatalytic oxidation of ethanol [33]. However, the energy unevenness of the surface of the dendrites causes a different speed of the galvanic substitution process (1). Thus, the highest density of filling with silver nanoparticles and their agglomerates is observed on the ribs (Fig. 7). Moreover, this regularity is observed regardless of the geometry of copper nanodendrites.
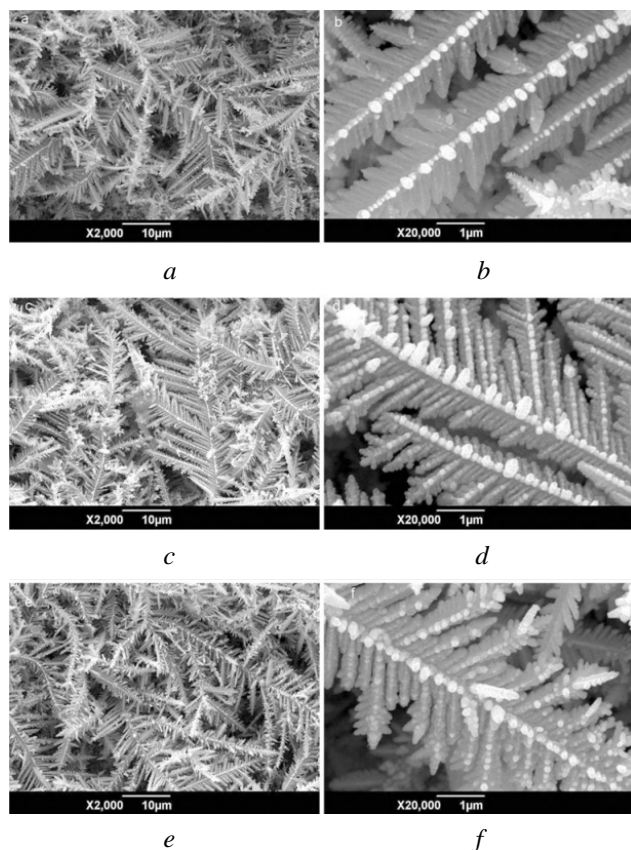

Fig. 7. Typical SEM images of Ag–Cu nanostructures obtained at different Cu ion deposition potentials: a, b – 0.6; c, d – 0.7 and e, f – 0.8 V versus SCE. The electrolysis time is 600 s, Ag ion concentration is 10mM, and the displacement reaction time is 10 min [23]

The authors of [26] established that the current density of reduction of carbon (IV) oxide on porous copper samples modified with nanosized silver is three times greater than the density of reduction on smooth copper and twice that on porous ones (according to $E = –1$ V). Therefore, the porous copper surface modified with nanosized silver due to the higher permeability of the electrolyte is characterized by significantly higher catalytic activity compared to the brass surface and the porous copper surface, and it can be used as a catalytically active cathode in the electroreduction of CO_2 in $KHCO_3$ solution.

Electrolytic porous copper and copper dendrites, despite the large specific surface area, are characterized by low mechanical strength. Therefore, they cannot always be used as substrates for decorating 3D electrodes with nanoparticles. Therefore, sacrificial substrates based on copper nanofibers [28], an array of nanotubes [34], and nanowires [35] are promising in this regard. In addition to a large specific surface area, they have high performance characteristics due to mechanical durability. Galvanic replacement on such substrates takes place with uniform deposition of nanoparticles on the side surface of nanothreads (Fig. 8). This is explained by the energy homogeneity of the cylindrical surfaces of copper nanowires and nanotubes.
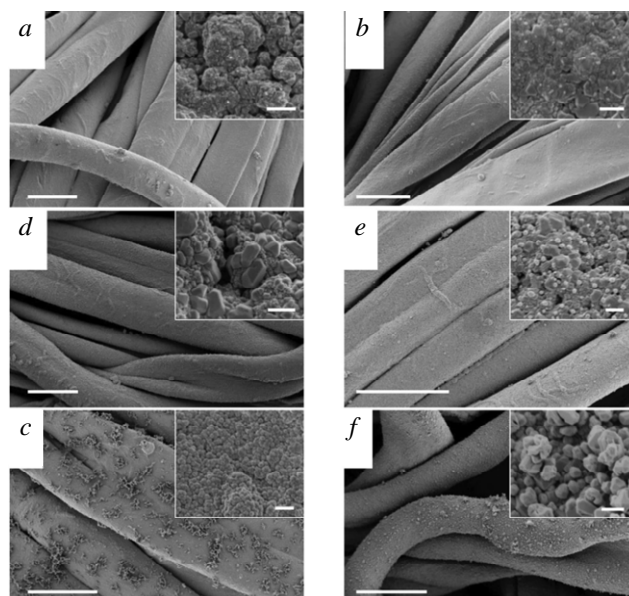

Fig. 8. SEM images obtained from the bimetallic Cu-Mx@Fabrics after GR reactions: a – Cu-Au10@Fabric; b – Cu-Au100@Fabric; c – Cu-Au1000@Fabric; d – Cu-Ag10@Fabric; e – Cu-Ag100@Fabric; and f – Cu-Ag1000@Fabric. Scale bars correspond to 20 µm for the main figure and 200 nm for the inset [28]

The effectiveness of the combination of the binary PdPt system deposited by galvanic substitution on electrolytic copper foam is shown on the example of the electrochemical production of hydrogen in a sulfuric acid solution (Fig. 9). Comparing the values of cathodic

currents on decorated and undecorated copper, it can be seen that the latter is catalytically less active and practically performs the function of only a substrate. The authors of [29] showed that $Pd_{65}Pt_{35}$ NFC is superior to Pt NFC in terms of electrocatalytic activity by approximately 1.5 times, which is due to higher permeability of the electrolyte and lower cost. The binary system also showed high stability during long-term electrolysis.
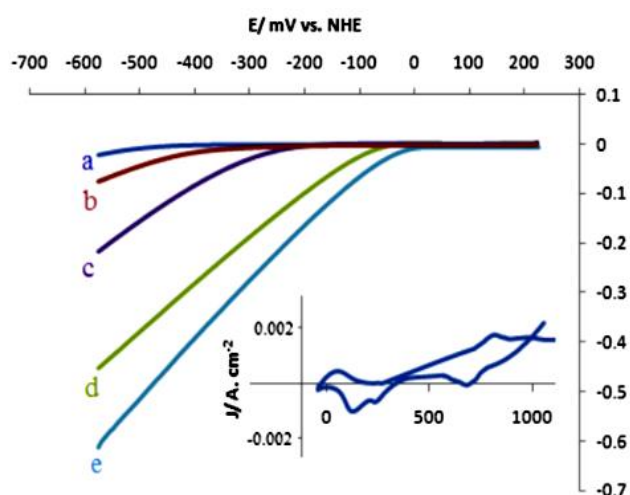

Fig. 9. LSVs of: a – bare Cu electrode; b – Cu nanofoam; c – Pd NFC; d – Pt NFC; e – $Pd_{65}Pt_{35}$ NFC in 0.5 M H_2SO_4 solution at scan rate 50 mV/s^{-1}. Inset: CVA for $Pd_{65}Pt_{35}$ NFC in 0.5 M H_2SO_4 solution [29]

Conclusions

3D metal surfaces are characterized by a large BET surface area, which determines their unique functional properties. Decoration of such materials with nanoparticles of metals and nanostructures and bimetals contribute to synergism, which is most observed in electrochemical catalysis. One of the technologically effective methods of applying MNPs to a 3D metal substrate is the galvanic replacement process. The latter is most studied on nickel and copper substrates with a large specific surface – foams, metals with submicron pores, nanodendrites and nanofibrous structures. Most often, decoration is carried out by noble metals (silver, gold, palladium, platinum), which ensure high catalytic activity and operational stability of decorated 3D materials. These metals are characterized by high values of standard electrode potentials, which provides a large electromotive force (DE) of the process of galvanic substitution in solutions of their precursors. Accordingly, it contributes to the formation of MNPs

and their nanostructures of these metals on 3D substrates.

References

1. Hassan, I. U., Salim, H., Naikoo, G. A., Awan, T., Dar, R. A., Arshad, F., Tabidi, M. A., Das, R., Ahmed, W., Asiri, A. M., Qurashi, A. H. (2021). A review on recent advances in hierarchically porous metal and metal oxide nanostructures as electrode materials for supercapacitors and non-enzymatic glucose sensors. *Journal of Saudi Chemical Society,* 25, 101228. https://doi.org/10.1016/j.jscs.2021.101228

2. Huang, A., He, Y., Zhou, Y., Zhou, Y., Yang, Y., Zhang, J., Luo, L., Mao, Q., Hou, D., Yang, J. (2019). A review of recent applications of porous metals and metal oxide in energy storage, sensing and catalysis. *Journal of Materials Science*, 54, 949–973. https://doi.org/10.1007/s10853-018-2961-5

3. Nakajima, H. (2019). Fabrication, Mechanical and Physical Properties, and Its Application of Lotus-Type Porous Metals. *Materials Transactions*, 60, 2481–2489. https://doi.org/10.2320/matertrans.MT-M2019182

4. Chen, J., Wang, Y., Li, S., Chen, H., Qiao, X., Zhao, J., Ma, Y., Alshareef, H. N. (2023). Porous Metal Current Collectors for Alkali Metal Batteries. *Advanced Science*, 10, 2205695. https://doi.org/10.1002/advs.202205695

5. Wang, Z., Zhao, Y. (2023). Porous Nickel Electrode for Highly Sensitive Non-Enzyme Electrochemical Glucose Detection. *Coatings*, 13, 290. https://doi.org/10.3390/coatings13020290

6. Zhu, P., Wu, Z., Zhao, Y. (2019). Hierarchical porous Cu with high surface area and fluid permeability. *Scripta Materialia*, 172, 119–124. https://doi.org/10.1016/j.scriptamat.2019.07.019

7. Fujita, T., Kanoko, Y., Ito, Y., Chen, L., Hirata, A., Kashani, H., Iwatsu, O., Chen, M. (2015). Nanoporous Metal Papers for Scalable Hierarchical Electrode. *Advanced Science*, 2, 1500086. https://doi.org/10.1002/advs.201500086

8. Hatamie, A., Rezvani, E., Rasouli, A.S., Simchi, A. (2018). Electrocatalytic Oxidation of Ethanol on Flexible Three-dimensional Interconnected Nickel/Gold Composite Foams in Alkaline Media. *Electroanalysis*, 30, 1–9. https://doi.org/10.1002/elan.201800490

9. Wang, Y., Niu, C., Zhu, Y. (2019). Copper-Silver Bimetallic Nanowire Arrays for Electrochemical Reduction of Carbon Dioxide. *Nanomaterials*, 9, 173. https://doi.org/10.3390/nano9020173

10. Yu, J., Shen, M., Liu, S., Li, F. Sun, D., Wang, T. (2017). A simple technique for direct growth of Au into a nanoporous alumina layer on conductive glass as a reusable SERS substrate. *Applied Surface Science*, 406, 285–293. https://doi.org/10.1016/j.apsusc.2017.02.103

11. Tamašauskaitė-Tamašiūnaitė, L., Zabielaitė, A., Balčiūnaitė, A., Šebeka, B., Stalnionienė, I., Buzas, V., Mačiulis, L., Tumonis, L., Norkus, E. (2017). Deposition of Pt Nanoparticles on Ni Foam via Galvanic Displacement. *Journal of The Electrochemical Society*, 164, D53–D56. https://doi.org/10.1149/2.0601702jes

12. Rizk, M. R., Abd El-Moghny, M. G. (2020). Controlled galvanic decoration boosting catalysis: Enhanced glycerol electro-oxidation at Cu/Ni modified macroporous films. *International Journal of Hydrogen Energy*, 10, 645–655. https://doi.org/10.1016/j.ijhydene.2020.10.004

13. Zavatski, S., Popov, A. I., Chemenev, A., Dauletbekova, A., Bandarenka, H. (2022). Wet Chemical Synthesis and Characterization of Au Coatings on Meso- and Macroporous Si for Molecular Analysis by SERS Spectroscopy. *Crystals*, 12, 1656. https://doi.org/10.3390/cryst12111656

14. 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. https://doi.org/10.3389/fchem.2019.00085

15. Zozulia, H. I., Kuntyi, O. I. (2019). Preparing of metallic electrocatalytic nanostructured surface by galvanic replacement method. Review. *Chemistry, Technology and Application of Substances*, 2, 25–34. https://doi.org/10.23939/ctas2019.02.025

16. Kuntyi, O. I., Zozulya, G. I., Shepida, M. V. (2020). Nanoscale galvanic replacement in non-aqueous media: a mini review. *Voprosy khimii i khimicheskoi tekhnologii*, 4, 5–15. https://doi.org/10.32434/0321-4095-2020-131-4-5-15

17. Kuntyi, O. I., Zozulya, G. I., Shepida, M. V., Nichkalo, S. I. (2019). Deposition of nanostructured metals on the surface of silicon by galvanic replacement: a mini-review. *Voprosy khimii i khimicheskoi tekhnologii*, 3, 74–82. https://doi.org/10.32434/0321-4095-2019-124-3-74-82

18. Niu, X., Xiong, Q., Li, X., Zhang, W., He, Y., Pan, J., Qiu, F., Yan, Y. (2017). Incorporating Ag into Pd/Ni Foam via Cascade Galvanic Replacement to Promote the Methanol Electro-Oxidation Reaction. *Journal of The Electrochemical Society*, 164, F651–F657. https://doi.org/10.1149/2.1551706jes

19. Verlato, E., He, W., Amrane, A., Barison, S., Floner, D., Fourcade, F., Geneste, F., Musiani, M., Seraglia, R. (2016). Preparation of Ag-modified Ni foams by galvanic displacement and their use as cathodes for the reductive dechlorination of herbicides. *ChemElectroChem*, 3, 2084–2092. https://doi.org/10.1002/celc.201600214

20. Kamyabi, M. A., Jadali, S. (2021). A sponge like Pd arrays on Ni foam substrate: Highly active non-platinum electrocatalyst for methanol oxidation in alkaline media. *Materials Chemistry and Physics*, 257, 123626. https://doi.org/10.1016/j.matchemphys.2020.123626

21. Kutyła, D., Nakajima, K., Fukumoto, M., Wojnicki, M., Kołczyk-Siedlecka, K. (2023). Electrocatalytic Performance of Ethanol Oxidation on Ni and Ni/Pd Surface-Decorated Porous Structures Obtained by Molten Salts Deposition/Dissolution of Al-Ni Alloys. *International Journal of Molecular Sciences*, 24, 3836. https://doi.org/10.3390/ijms24043836

22. Schichtl, Z. G., Mehrabi, H., Coridan, R. H. (2020). Electrooxidation of Glycerol on Self-Organized, Mixed Au–Pt Interfaces Formed on Ni Substrates. *Journal of The Electrochemical Society*, 167, 056502. https://doi.org/10.1149/1945-7111/ab679e

23. 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. https://doi.org/10.1007/s10800-013-0563-0

24. Rahmatolahzadeh, R., Ebadi, M., Motevalli, K. (2017). Preparation and characterization of Cu clusters and Cu–Ag alloy via galvanic replacement method for azo dyes degradation. *Journal of Materials Science: Materials in Electronics*, 28, 6056–6063. https://doi.org/10.1007/s10854-016-6281-8

25. Wang, C., Wang, C., Xiong, Z., Wang, J., Zhang, W., Shi, H., Wang, D., Gu, Y., Bai, Z., Gao, Y., Yan, X. (2022). Silver modified copper foam electrodes for enhanced reduction of CO_2 to C_{2+} products. *Materials Advances*, 3, 4964–4972. https://doi.org/10.1039/d2ma00188h

26. Zozulya, G. I., Kuntyi, O. I., Mertsalo, I. P., Mazur, A. S. (2021). Production of Cu/Ag porous bimetal by the galvanic replacement of dezincified brass. *Materials Science*, 56, 668–672. https://doi.org/10.1007/s11003-021-00480-y

27. 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 Reduction. *Nanomaterials*, 8, 756. https://doi.org/10.3390/nano8100756

28. Anderson, S. R., O'Mullane, A. P., Gaspera, E. D., Ramanathan, Bansal, R. V. (2019). LSPR-Induced Catalytic Enhancement Using Bimetallic Copper Fabrics Prepared by Galvanic Replacement Reactions. *Advanced Materials Interfaces*, 1900516. https://doi.org/10.1002/admi.201900516

29. Rezaei, B., Mokhtarianpour, M., Ensafi, A. A. (2015). Fabricated of bimetallic Pd/Pt nanostructure deposited on copper nanofoam substrate by galvanic

replacement as an effective electrocatalyst for hydrogen evolution reaction. *International Journal of Hydrogen Energy*, 40, 6754–6762. http://dx.doi.org/10.1016/j.ijhydene.2015.03.122

30. Nitopi, S., Bertheussen, E., Scott, S. B., Liu, X., Engstfeld, A. K., Horch, S., Seger, B., Stephens, I. E. L., Chan, K., Hahn, C., Nørskov, J. K., Jaramillo, T. F., Chorkendorff, I. (2019). Progress and Perspectives of Electrochemical CO_2 Reduction on Copper in Aqueous Electrolyte. *Chemical Reviews*, 119, 7610–7672. https://doi.org/10.1021/acs.chemrev.8b00705

31. Li, C. W., Kanan, M. W. (2012). CO_2 Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu_2O Films. *Journal of the American Chemical Society*, 134, 7231−7234. https://doi.org/10.1021/ja3010978

32. Gnilitskyi, I., Bellucci, S., Marrani, A. G., Shepida, M., Mazur, A., Zozulya, G., Kordan, V., Babizhetskyy, V., Sahraoui, B., Kuntyi, O. (2023). Femtosecond laser-induced nano- and microstructuring of Cu electrodes for CO_2 electroreduction in acetonitrile medium. *Scientific Reports*, 13, 8837. https://doi.org/10.1038/s41598-023-35869-z

33. Abbasi, N., Shahbazi, P., Kiani A. (2013). Electrocatalytic oxidation of ethanol at Pd/Ag nanodendrites prepared via low support electrodeposition and galvanic replacement. *Journal of Materials Chemistry A*, 1, 9966–9972. https://doi.org/10.1039/c3ta10706j

34. Mohl, M., Dobo, D., Kukovecz, A., Konya, Z., Kordas, K., Wei, J., Vajtai, R., Ajayan, P. M. (2011). Formation of CuPd and CuPt Bimetallic Nanotubes by Galvanic Replacement Reaction. *The Journal of Physical Chemistry C*, 115, 9403–9409. https://doi.org/10.1021/jp112128g

35. He, X., He, R., Lan, Q., Duan, F., Xiao, J., Song, M., Zhang, M., Chen, Y., Li, Y. (2016). A Facile Fabrication of Silver-Coated Copper Nanowires by Galvanic Replacement. *Journal of Nanomaterials*, 2016, Article ID 2127980. http://dx.doi.org/10.1155/2016/2127980

Г. І. Зозуля[1], М. В. Шепіда[1], Ч. Гюшлютен[2], О. І. Кунтий[1]
[1] Національний університет "Львівська політехніка",
кафедра хімії і технології неорганічних речовин
[2] Науково-технологічний університет Адана Алпарслана Тюркеша, Туреччина

ДЕКОРУВАННЯ 3D ПОВЕРХНІ НІКЕЛЮ ТА МІДІ МЕТАЛЕВИМИ НАНОЧАСТИНКАМИ ТА НАНОСТРУКТУРАМИ ГАЛЬВАНІЧНИМ ЗАМІЩЕННЯМ. МІНІОГЛЯД

Розглянуто ефективність методу гальванічного заміщення для декорування поруватої поверхні металевими наночастинками та наноструктурами. Показано, що залежно від функціонального призначення для модифікації гальванічним заміщенням переважно застосовують пінні, поруваті та дендритні металеві 3D субстрати. Зокрема це нікелеві та мідні субстрати, на які осаджують noble metals. Наведено особливості формування нанорозмірних осадів на поруватих мідній і нікелевій поверхнях залежно від структури останніх та умов гальванічного заміщення. Зазначено основні сфери їх застосування.

Ключові слова: пористі метали; піна; нанодендрит; гальванічна заміна; металеві наночастинки; наноструктури; поверхні нікелю та міді.