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SYNTHESIS OF BIMETALLIC NANOSTRUCTURES ON A SACRIFICIAL SILVER NANOTEMPLATE BY GALVANIC REPLACEMENT. REVIEW

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The current state of research on the formation of bimetallic nanostructures by galvanic replacement is presented. The effectiveness of galvanic replacement for the controlled synthesis of Au/Ag, Pd/Ag, and Pt/Ag on a silver nanotemplate in aqueous solutions is shown. The features of morphological and structural transformations of sacrificial nanosilver at various replacement stages are discussed. The dependencies of the geometry and composition of Au/Ag, Pd/Ag, and Pt/Ag nanostructures on the main parameters of galvanic replacement – such as the nature and concentration of the reducible metal ions, the ratio between the silver nanotemplate and the metal precursor, the duration of the process, and the temperature – are analysed. Accents are made on a comprehensive approach to their influence for the controlled synthesis of Au/Ag, Pd/Ag, and Pt/Ag nanostructures with predetermined characteristics.

Keywords: silver nanotemplate, galvanic replacement, metal nanoparticles, bimetallic nanostructures, hollow nanoparticles.

Introduction

The synthesis of metallic nanostructures on a sacrificial nanotemplate is one of the promising directions for applying galvanic (contact) replacement (GR) [1–3]. The processes of nanoscale GR have been systematically studied since 2002 [4]. They provide a universal and controlled synthesis of various metallic nanostructures with specific compositions and geometries [5, 6]. Galvanic replacement is primarily used to obtain hollow nanostructures (nanoboxes, nanoframes, nanocages) and core-shell structures. Such nanostructures are characterized by unique properties (catalytic [1, 3, 5], optical [1, 7]), which determine a wide range of their applications in chemical and electrochemical catalysis, plasmonics and biomedicine.

Nanoscale galvanic replacement is characterized by the following: 1) the replacement between a metallic nanoparticle (sacrificial template) and another metal precursor (with a higher standard reduction potential) occurs spontaneously; 2) the process is quite universal and can be adapted to almost any sacrificial metallic nanoparticles and salt precursors; 3) the method represents a simple route for the controlled formation of nanostructures with ultrathin walls in only one step, where the composition of the synthesized nanoparticles can be easily controlled by adjusting the ratio of the sacrificial template to the metal precursor.

The reaction of nanoscale galvanic replacement occurs via an electrochemical mechanism [1, 2] and leads to the deposition of metal M_2 with a lower equilibrium electrode potential onto the template nanoparticle of metal M_1, which has a higher equilibrium electrode potential.

$$mM_1^{n+} + nM_2 \text{ « } mM_1 + nM_2^{m+}. \qquad (1)$$

The design of metallic nanostructures and their functional properties depend on the main factors of nanoscale galvanic replacement: the nature of the nanoscale sacrificial template and the deposited metal; the composition of the solution (concentration of ions of the reduced metal, the ratio between the nanotemplate and the precursor, surfactants); the nature of the medium (aqueous or non-aqueous), temperature, and process duration. In the aspect of controlled synthesis of metallic nanostructures with predetermined characteristics, the complex influence of factors of their formation is considered. Most of the research on nanostructure synthesis via galvanic replacement focus on transforming various Ag nanoparticles into more complex bimetallic nanostructures [7–11] with unique functional properties.

The aim of this work is to analyse the scientific literature on the features of forming bimetallic nanostructures Au/Ag, Pd/Ag, and Pt/Ag on sacrificial silver nanotemplates in aqueous solutions via galvanic replacement.

1. Synthesis of Au/Ag nanostructures

Nanoscale galvanic replacement is a spontaneous and multifactorial process. In the aspect of controlled synthesis of metallic nanostructures with predetermined characteristics, the complex influence of their formation factors is considered. The main synthesis conditions of bimetallic Au/Ag nanostructures on the Ag surface in aqueous solutions by galvanic replacement [4, 7–25] are presented in Table 1.

Au/Ag nanostructures are synthesised by galvanic replacement on sacrificial silver nanotemplates in an $H[AuCl_4]$ solution according to reaction (2) [4, 7–11, 14–25]. Their composition and structure can be easily controlled by regulating the molar ratio between Ag nanoparticles (AgNPs) and the $[AuCl_4]^-$ precursor. Morphological and structural changes at different stages of this process are shown in Fig. 1.

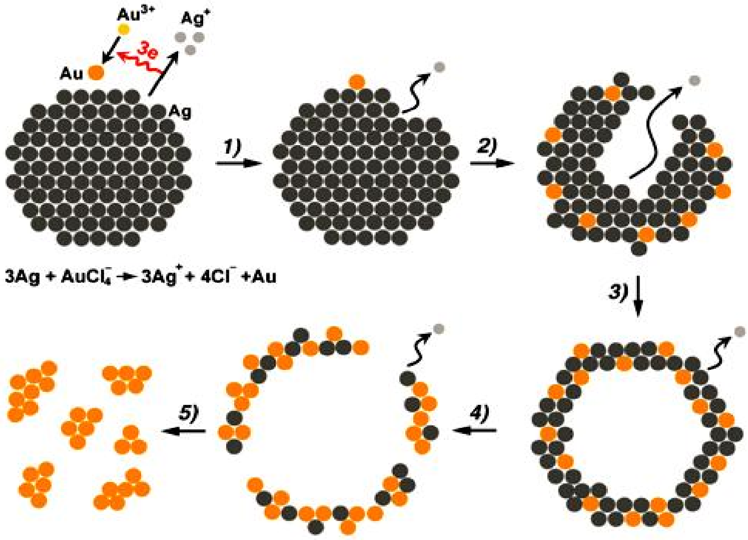


Fig. 1. Scheme of the morphological and structural changes at different stages of galvanic replacement between an Ag nanoparticle and an aqueous H[AuCl₄] solution [5]

$$3Ag + [AuCl_4]^- \rightarrow Au + 3AgCl + Cl. \qquad (2)$$

When an aqueous solution of $H[AuCl_4]$ comes into contact with a suspension of AgNPs, galvanic replacement immediately begins at regions with the highest surface energy (e.g., defect, protrusion, irregularities). Ag atoms oxidise and dissolve, forming a small cavity on the nanoparticle surface. At the same time, the generated electrons rapidly migrate across the nanoparticle surface and reduce near-surface $[AuCl_4]^-$ ions from the solution. The newly formed Au atoms tend to deposit epitaxially on the Ag nanoparticle surface (Fig. 1, stage 1) due to the similar face-centred cubic crystal structures and lattice constants of gold and silver (gold = 4.079 Å; silver = 4.086 Å) [4]. This leads to the formation of a thin, incompact layer of gold on the surface of each nanoparticle, which does not interfere the inner layers of Ag from reacting with the $[AuCl_4]^-$ precursor. Over time, the small cavities on the nanoparticle surface become the main sites for template dissolution, providing the diffusion of reactive species.

Along with the deposition of Au, alloying of the main Ag occurs (stage 2) because a homogeneous alloy is thermodynamically more stable than a mixture of Au and Ag [5]. Complete dissolution of the sacrificial Ag transforms the nanoparticle into a hollow nanostructure with an alloyed shell (stage 3). Moreover, the thickness of the shell and the size of the voids depend on the size of the sacrificial nanotemplate and the stoichiometric ratio between Ag and Au(III). Adding $H[AuCl_4]$ to the reaction system leads to the splitting of the Au/Ag shell by selectively removing Ag atoms and forming porous nanostructures (stage 4) and Au nanoparticles (stage 5) [24].

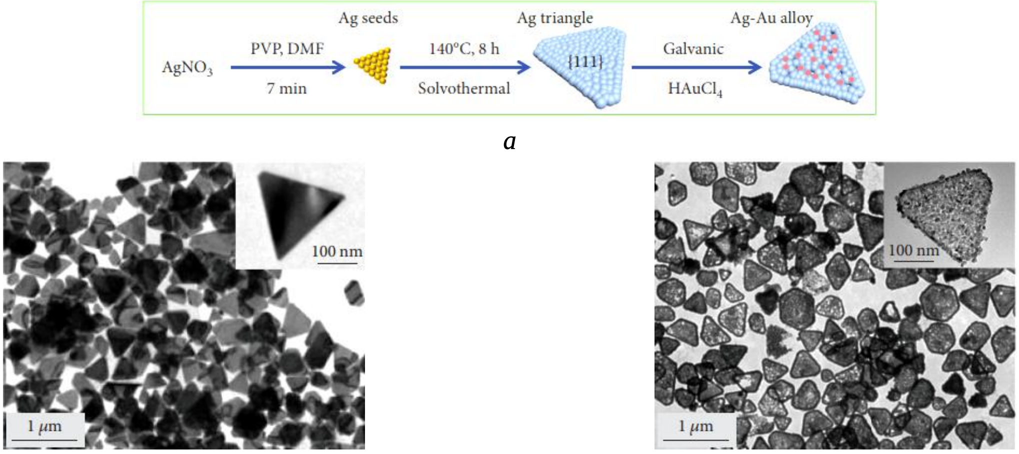
To stabilise the synthesised Au/Ag nanostructures, solutions of PVP (polyvinylpyrrolidone) [7, 9, 10, 13, 14, 17–19, 21, 24, 25], CTAB (cetyltrimethylammonium bromide) [11] are used. Stabilised nanospheres [7, 19, 20], nanocubes [24], nanoprisms [26], and nanowires [27] serve as sacrificial silver templates.

Table 1

Conditions for the formation of Au/Ag nanostructures
on a sacrificial silver nanotemplate by galvanic replacement

Silver nanotemplate	Solution composition	t, °C	t	Size of NPs, nm	Characteristic of NPs	Refs.
AgNPs	$HAuCl_4$	100	10 min	~40	AuAg NPs	[4]
Ag nanospheres	0.5 mM $HAuCl_4$, PVP + + formaldehyde	20	24 h	65–115	AgAu hollow nanoparticles	[7]
AgNPs nanopillars	$HAuCl_4$	20	10, 30, 60 min	103.6 ± 29.8, 145.6 ± 49.6	Nanoscale cracks and hollows in Au/AgNPs	[8]
smooth triangular Ag nanoplates	0.2 mM $HAuCl_4$ + PVP	100	30 min	40	roughened nanoporous Ag-Au triangular nanoprisms	[9]
AgNPs	$HAuCl_4$ + PVP	100	10 min	48.0±2.1, 3.3±0.3	hollow nanoplates Au/Ag	[10]
AgNPs nanoplates	1 mM $HAuCl_4$ CTAB	20	2 h	80–100	nanoplates Au/Ag	[11]
AgNPs	$HAuCl_4$ + NaBr $HAuCl_4$ $AuBr_2^-$, $AuCl_4^-$	100	20 min	50	Au–Ag nanoshells, porous Au–Ag nanoframes, Au@Au–Ag nanorattles	[12]
Ag nanoplates	Au(I) + PVP $Na_3Au(SO_3)_2$	20	30 min	30–40	triangular holey Au–Ag alloy nanoframes	[13]
AgNPs	2.94 mM $HAuCl_4$ + + 10 mM ascorbic acid + + PVP	20	5 min	95±15	hollow urchin-like Au/Ag AuNPs	[14]
Ag nanoplates	$HAuCl_4$	20	5 min	40	Au/Ag nanoframes	[15]
triangular Ag nanoplates	1 mM $HAuCl_4$	20	72 h	10–40	nanorings, nanocages, or hollow nanoplates Au/Ag	[16]
hexagonal Ag nanoplates	0.2 mM $HAuCl_4$ + PVP	100	10 min	120	hex nut shaped Au–Ag nanostructures	[17]
AgNPs	1 mM $HAuCl_4$ + + 5 mM PVP + HCl	20	60 s	60–150	AuAg Nanoshells	[18]
spherical AgNPs	0.2 mM $HAuCl_4$ + PVP	100	10 min	30–40	spherical hollow Au–Ag NPs	[19]
Ag nanospheres	3.4×10^{-4} M $HAuCl_4$	20	6 h	11.4 ± 1.4	hollow nanospheres AuAg NPs	[20]
AgNPs nanoboxes	0.5 mM $HAuCl_4$ + PVP	0–105	20 min	30–50	porous nanoboxes Ag/Au	[21]
AgNPs nanoshells	0.2 mM $HAuCl_4$	100	10 min	3–10	porous nanoshells Au/Ag	[22]
AgNPs	169 mM $HAuCl_4$ + NaCl, NaBr, KI	100	30 min	20–50	hollow Au/AgNPs	[23]
Ag nanocubes	0.1 mM $HAuCl_4$ + + PVP, AuCl + PVP	23–90	1–5 min	40–70	hollow nanoboxes Au/Ag	[24]
AgNPs	0.1 mM $HAuCl_4$, 0.1 mM AuCl, 0.1 mM $KAuBr_4$ PVP	20	10 min	~50	hollow Au/AgNPs	[25]

During the synthesis process of nanostructures by galvanic replacement, the main characteristic of the final structure is the morphology of the transformed matrix. Accordingly, the shape of the synthesised Au/Ag nanostructures corresponds to the shape of the sacrificial template [9, 11]. For example, galvanic replacement between smooth triangular Ag plates and $[AuCl_4]^-$ ions results in the formation of rough, nanoporous bimetallic triangular Ag-Au nanoprisms (Fig. 2).



a

b

c

Fig. 2. Schematic representation of synthesizing Ag nanoplates and Ag-Au TNPs (a). TEM images of Ag nanoplates (b) and Ag-Au TNPs (c) [9]

The transformation of the sacrificial nanotemplate depends on its initial configuration [4, 5, 28]. The morphological changes of monocrystalline Ag nanocubes and truncated Ag nanocubes during nanoscale galvanic replacement with an aqueous $H[AuCl_4]$ solution differ significantly (Fig. 3). On nanocubes, anodic regions appear on their faces, which causes the formation of point-like holes (Fig. 3, *a*–*e*). If the Ag nanocubes have truncated corners, dissolution occurs in the {111} planes of each corner, forming Au/Ag nanostructures with uniform, evenly distributed pores at the corners of the particles (Fig. 3, *f*–*j*). The difference in nanostructure formation is due to the more effective binding properties of the stabilising polymer on the {100} faces of the truncated nanostructures.

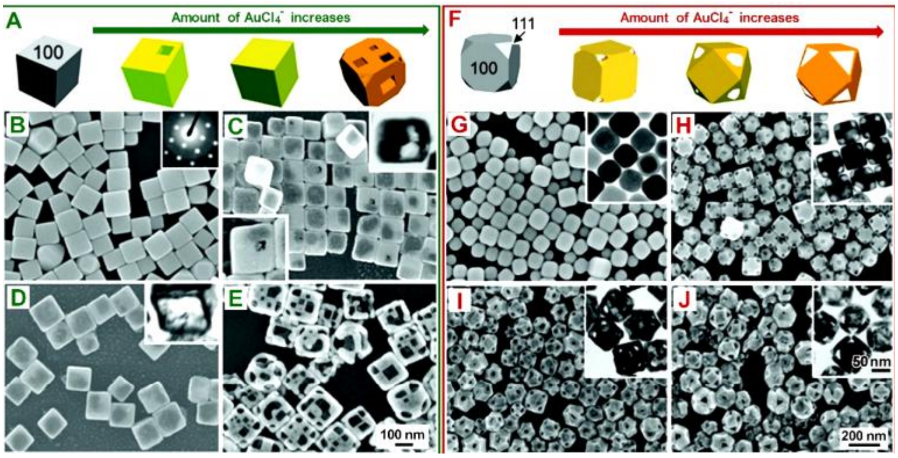


Fig. 3. (A) Scheme of the structural evolution of an Ag nanocube by galvanic replacement with $AuCl_4^-$. SEM and (inset) TEM images of (B) Ag nanocubes and Au/Ag nanostructures prepared from (C) 0.3, (D) 0.5, and (E) 2.25 mL of 1 mM $HAuCl_4$. (F) Schematic representation of the structural evolution of an Ag nanocube with truncated corners by replacement with $AuCl_4^-$. SEM and (inset) TEM images of (G) an Ag nanocube and Au-Ag nanostructures prepared from (H) 0.6, (I) 1.6, and (J) 3.0 mL of 0.1 mM $HAuCl_4$ [28]

Hollow bimetallic nanostructures with complex shapes and unique functional properties are also synthesised by galvanic replacement. The authors [17] proposed the synthesis of Au/Ag nanostructures in the shape of a hexagonal nut by nanoscale galvanic replacement between hexagonal Ag nanoplates (122 nm thick) and an aqueous H[$AuCl_4$] solution (Fig. 4). Unlike other Ag nanostructures (e.g., nanocubes), which provide the formation of hollow nanostructures that replicate the template's morphology, the Ag nanoplate was directly transformed into a porous nanostructure in the shape of a hexagonal nut. The pore size and density were controlled by varying the molar ratio of H[$AuCl_4$] and Ag. These hexagonal porous metallic nanostructures have potential applications in biomedicine as contrast agents or therapeutic agents.

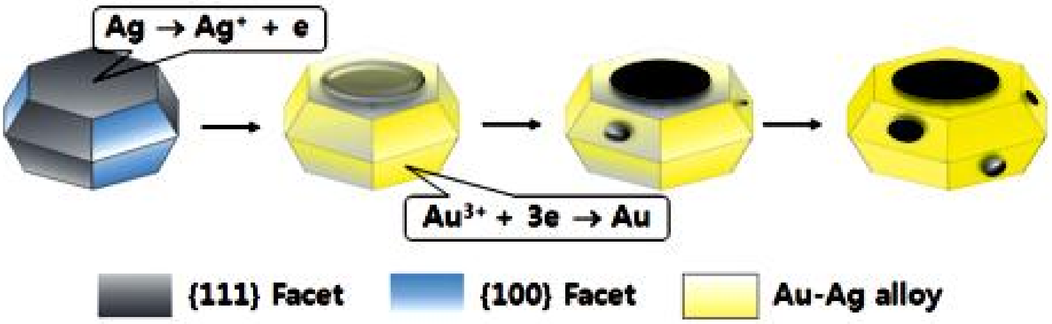


Fig. 4. Scheme of the formation of Au/Ag nanostructures having a hex nut shape [17]

Adjusting the parameters of nanoscale galvanic replacement can lead to the deformation of the initial template and the formation of various nanostructures. For example, by regulating the pH of an aqueous H[$AuCl_4$] solution, nanoparticles, nanorings, and nanocages can be synthesised [16]. During dissolution, H[$AuCl_4$] gradually hydrolyses to $[AuCl_x(OH)_{4-x}]^-$, (x = 0…4). At different pH levels, the concentrations of hydrolysed Au complexes in the solution are different (Fig. 5). However, as the pH increases, the value of x gradually decreases, and the overall standard potential of the Au precursor solution also decreases (equations 3–7). Therefore, slight adjusttments to the pH can regulate the driving force of galvanic replacement and, accordingly, the morphology of the formed nanostructures. At pH below 7, silver nanostructures break down rapidly, forming heterogeneous colloidal gold particles during galvanic replacement. At higher pH, triangular nanostructures and nanocages are formed.

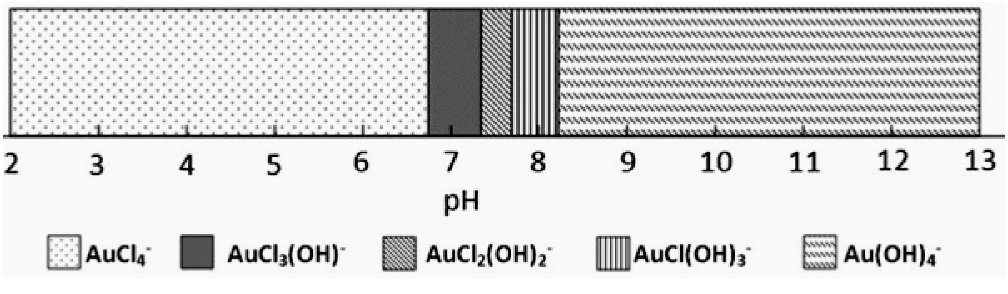


Fig. 5. pH ranges of the presence of ions of Au complexes in solution [16]

$$[AuCl_4]^- + 3e \leftrightarrow Au + 4Cl^- \; E^0 = 1.004 \text{ V}, \tag{3}$$

$$[AuCl_3(OH)]^- + 3e \leftrightarrow Au + 3Cl^- + OH^- \; E^0 = 0.889 \text{ V}, \tag{4}$$

$$[AuCl_2(OH)_2]^- + 3e \leftrightarrow Au + 2Cl^- + 2OH^- \; E^0 = 0.785 \text{ V}, \tag{5}$$

$$[AuCl(OH)_3]^- + 3e \leftrightarrow Au + Cl^- + 3OH^- \; E^0 = 0.689 \text{ V}, \tag{6}$$

$$[Au(OH)_4]^- + 3e \leftrightarrow Au + 4OH^- \; E^0 = 0.602 \text{ V}. \tag{7}$$

For controlled galvanic replacement of Ag nanoparticles, in addition to traditional Au(III) chloride precursors, Au(I) sulfite complexes $Na_3[Au(SO_3)_2]$ [13], Au(I) chloride (AuCl), $K[AuBr_4]$ [25], and $[AuBr_2]^-$ solutions [12] are also used. The latter are obtained by ion exchange between $[AuCl_4]^-$ and a stoichiometric amount of Br^-, followed by the reduction of $[AuBr_4]^-$. This method inhibits Au^+ disproportionation, providing the colloidal stability of Ag nanoparticles during the replacement reaction. A comparative study of the structural evolution of Ag nanoparticles during galvanic replacement with $[AuBr_2]^-$ and $[AuCl_4]^-$ demonstrates that uniform Au/Ag nanoshells are gradually formed using Au(I), whereas porous Au/Ag nanoframes are generated with Au(III). Moreover, more complex Au@Au-Ag nanostructures can be synthesised in $[AuBr_2]^-$ solutions.

Bimetallic nanostructures obtained by galvanic replacement typically have low Au/Ag ratios and, accordingly, are highly unstable. This may be due to their high tendency to decompose by excess $H[AuCl_4]$ [5, 29]. This limits their use in many corrosive conditions. The low Au/Ag ratio is largely due to the stoichiometry of the galvanic replacement: with $H[AuCl_4]$ as the Au source, only one Au atom can be formed during the removal of three Ag atoms (2). As a result, the growth rate of Au on Ag nanocrystals is much lower than the etching rate of Ag, leading to a low Au/Ag ratio of hollow nanostructures. One solution to this problem is the use of monovalent Au(I) salt as the Au source, which implies the addition of one Au atom to remove one Ag atom [13, 25]. Specifically, the alternative Au(I) precursor $Na_3[Au(SO_3)_2]$ can rapidly increase the Au/Ag ratio and provide the formation of porous Au-Ag alloy nanoplates with high chemical stability (Fig. 6). However, the holey nanoplates obtained by galvanic replacement using $H[AuCl_4]$ are highly unstable and transform into hollow triangular nanoframes [13]. Thus, using Au(I) precursors instead of Au(III) provides more controlled galvanic replacement.

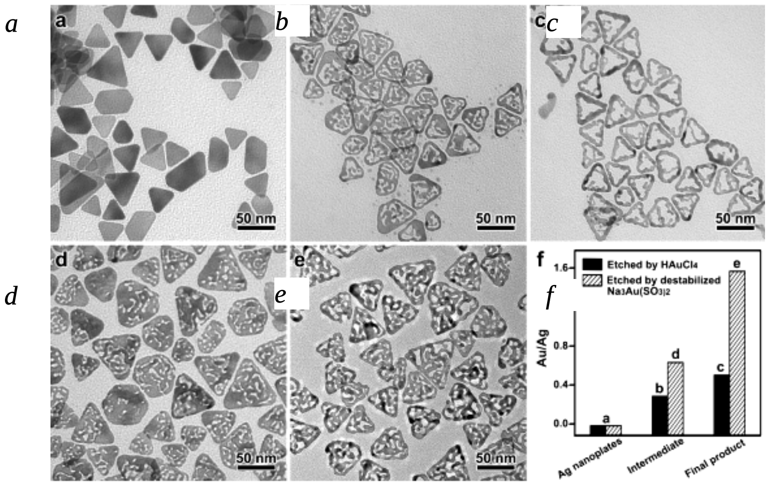


Fig. 6. Ag nanoplates (a); Holey Au-Ag alloy nanoplates (intermediate) and nanoframes (final product) formed by the galvanic replacement of Ag with $HAuCl_4$ (b–c); Holey Au-Ag nanoplates as intermediate and final products formed by the galvanic replacement of Ag with $Na_3Au(SO_3)_2$ (d–e); Evolution of the Au/Ag ratio in the Au-Ag alloy nanostructures (samples a–e) [13] (f)

The authors [23] demonstrated the ability to tune the size, shape, and composition of hollow Au/Ag nanostructures by galvanic replacement using various halide ions – chlorine, bromine, and iodine. Changing the NaCl concentration in the solution of prepared Ag nanoparticles before adding $H[AuCl_4]$ leads to precise tuning of the size and the core-to-cavity ratio of the obtained Au/Ag nanostructures according to the reaction (8). Cl^- ions, present in both $H[AuCl_4]$ and NaCl, slow down the reduction of gold, leading to more monodisperse hollow Au/Ag nanostructures. As the NaCl concentration increases, hollow Au/Ag nanostructures are formed by galvanic replacement with an increase in the shell thickness and a decrease in their external size.

$$3Ag + Cl^- + AuCl_4^- \rightarrow Au + 3AgCl + 2Cl^-. \quad (8)$$

By adding NaBr to the reaction solution, Br^- ions can easily replace Cl^- in the $[AuCl_4]^-$ precursors due to the higher stability constants of $[AuBr_4]^-$ compared to $[AuCl_4]^-$. Moreover, the presence of Br^- ions shifts the equilibrium to the right (9), additionally promoting galvanic replacement (10). The passage of such processes leads to the formation of heterogeneous hollow Au/Ag nanostructures. The polydispersity is caused by the partial interaction of NaBr with AgNPs and the formation of AgBr on the surface of the sacrificial nanoparticles.

$$[AuCl_4]^- + 4Br^- \rightarrow [AuBr_4]^- + 4Cl^-, \quad (9)$$

$$3Ag + [AuBr_4]^- \rightarrow Au + 3AgBr + Br^-. \quad (10)$$

By adding KI to AgNPs before introducing the gold precursor, AgI nanoparticles and spherical AuNPs are formed (11).

$$3Ag + 3I^- + [AuCl_4]^- \rightarrow Au + 3AgI + 4Cl^-. \quad (11)$$

Recent studies on the synthesis of Au/Ag nanostructures by galvanic replacement have focused on: providing high-yield production of monodisperse Au/Ag at room temperature with extended control of surface morphology, wall thickness, cavities size, and elemental composition; achieving high reproducibility of the process; mathematical modelling and optimization of multifactor galvanic replacement for the purpose of process controllability.

2. Synthesis of Pd/Ag and Pt/Ag nanostructures

In addition to bimetallic Au/Ag nanostructures, Pd/Ag nanostructures [26, 27, 30, 31] and Pt/Ag [32, 33] nanostructures are obtained by galvanic replacement in aqueous solutions on a sacrificial silver nanotemplate (Table 2). $[PdCl_4]^{2-}$, $PdCl_2$, $[PtCl_4]^{2-}$, $[PtCl_6]^{2-}$ are mainly used as precursors.

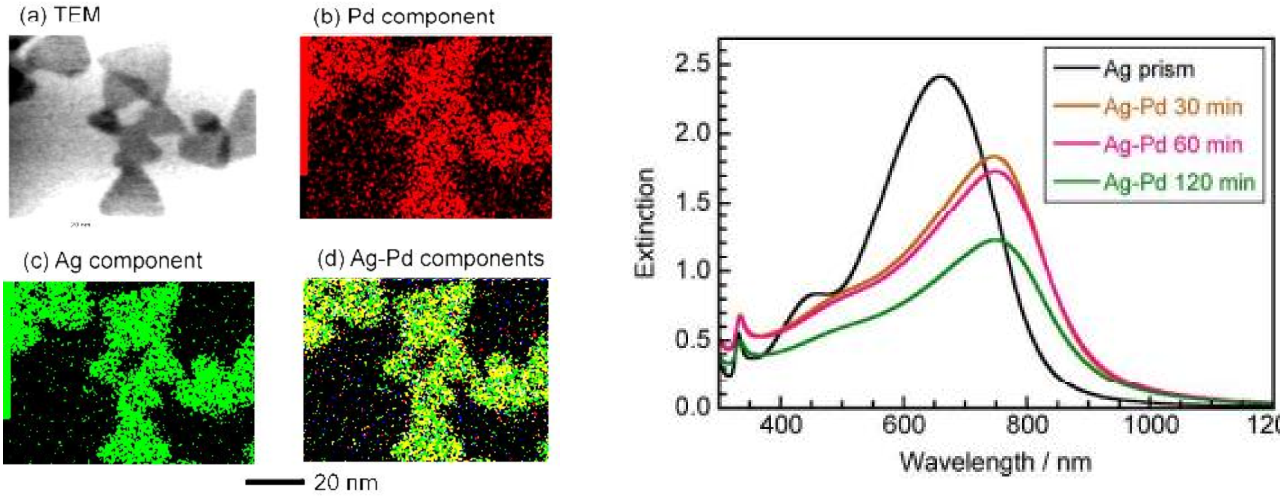
If the galvanic replacement of Ag nanoparticles in $[AuCl_4]^-$ solutions is spontaneous and kinetically fast, then the interaction of AgNPs with $[PdCl_4]^{2-}$ at room temperature does not occur for a long time. This is because the standard electrode potential of $PdCl_4^{2-}/Pd$ (0.591 V vs. SHE) is lower than that of Ag^+/Ag (0.800 V vs. SHE) [26, 30]. However, when the solution is heated to 100 °C, $PdCl_4^{2-}$ ions can thermally decompose to form Pd^{2+}. The standard reduction potential of Pd^{2+}/Pd is 0.951 V (vs. SHE), i.e. more positive than Ag^+/Ag, which makes galvanic replacement thermosdynamically possible according to equations 12–14 [26]. Increasing the reaction temperature kinetically promotes interdiffusion between Ag and Pd atoms, facilitating the synthesis of hollow nanostructures.

$$2Ag \rightarrow 2Ag^+ + 2e, \quad (12)$$

$$Pd^{2+} + 2e \rightarrow Pd, \quad (13)$$

$$Pd^{2+} + 2Ag \rightarrow Pd + 2Ag^+ \ \Delta E^0 = 0.12 \text{ V}. \quad (14)$$

Triangular Pd/Ag alloy plates slowly form by adding $Na_2[PdCl_4]$ and heating at 100 °C for 30–120 min (Fig. 7). The results indicate that additional treatment with a saturated NaCl solution is effective in transforming the Pd/Ag alloy nanoplates into hollow Pd/Ag nanoframes.



a *b*

Fig. 7. TEM and TEM-EDS images of Pd/Ag alloy triangular nanoplates produced by GR reaction after heating for 120 min (a); SPR band of Ag prisms and Pd/Ag alloy particles at different heating time (b) [26]

The authors [30] proposed the synthesis of Pd/Ag nanostructures by galvanic replacement in $H_2[PdCl_4]$ solutions at pH = 3, room temperature, and without adding any electrolytes or ligands containing Cl^- anions. Under these conditions, the $H_2[PdCl_4]$ solution consists of various Pd(II) species in equilibrium concentrations, with a significant fraction of Pd(II) existing in the form of Pd^{2+} ions, which thermodynamically enable the galvanic replacement reaction.

Pt/Ag nanostructures are mainly synthesized in aqueous $H_2[PtCl_6]$ solutions [32]. Since the standard electrode potential of $[PtCl_6]^{2-}/Pt$ (1.44 V (vs. SHE)) is higher than that of Ag^+/Ag (0.80 V (vs. SHE)), the galvanic replacement reaction (15) occurs spontaneously after the addition of H_2PtCl_6 to Ag nanoparticles.

$$4Ag + PtCl_6^{2-} \rightarrow Pt + 4AgCl + 2Cl^- . \qquad (15)$$

However, unlike Au/Ag and Pd/Ag nanostructures, Pt/AgNPs form over a long period of time – 12–48 h [32, 33]. For instance, galvanic replacement of Ag nanoprisms (40 nm) in an H_2PtCl_6 solution at room temperature for 24 h results in the formation of Pt/Ag alloy nanoprisms. After treating the reaction solution with saturated NaCl, the synthesized nanoprisms are transformed into Pt-enriched Pt/Ag alloy nanoframes. This method provides a simple technique for preparing catalytically active Pt/Ag alloys with a high Pt content (up to 97 %) [32].

Table 2

Conditions for the formation of Pd/Ag and Pt/Ag nanostructures on a sacrificial silver nanotemplate by galvanic replacement

Silver nanotemplate	Solution composition	t, °C	t	Size of NPs, nm	Characteristic of NPs	Refs.
AgNPs nanoprism	$HAuCl_4$ Na_2PdCl_4	20 100	10, 30–120 min	20–50	Triangular hollow nanoframes Ag–Au, Ag–Pd	[26]
Ag nanowires	0.294 mM $HAuCl_4$ 0.588 mM Na_2PdCl_4	5 20	12 h	~170, ~10	nanotubes Au@PdAg	[27]
Ag nanocubes	1 mM H_2PdCl_4+ + ascorbic acid, formaldehyde	20	1 h	80–100	hollow Pd/Ag NPs	[30]
AgNPs	$PdCl_2$	25	5 min	2–3	Pd/AgNPs	[31]
AgNPs nanoprism	H_2PtCl_6	20	12, 24, 36, 48 h	20–40, 5–7	triangular nanoframes Pt/Ag	[32]
Ag nanocubes	K_2PtCl_4	22±2	24 h	20	hollow AgPt NPs	[33]

Changing the reaction temperature during the synthesis of bimetallic nanoparticles by galvanic replacement can adjust their morphology and surface design, as it affects the reduction kinetics, nucleation/growth stages, and the possibility of alloyiing and the diffusion rate [34]. For instance, during galvanic replacement on AgNPs at room temperature, the formed Ag ions precipitate as AgCl crystals on the sacrificial nanosurface, further acting as templates for metal deposition from the precursor solution. This limits surface diffusion and leads to the formation of rough shells. At high temperatures (100 °C), AgCl precipitation does not occur (due to increased solubility) and smooth metallic Pt/Ag shells are formed on the surface of the sacrificial nanosilver (Fig. 8).

Bimetallic Pd/Ag and Pt/Ag nanostructures synthesized by galvanic replacement are characterized by high porosity, a large reactive surface area, and high catalytic activity due to the synergistic effect between their components [30–33]. These nanostructures are attractive in terms of their use in catalytic and electrocatalytic processes.

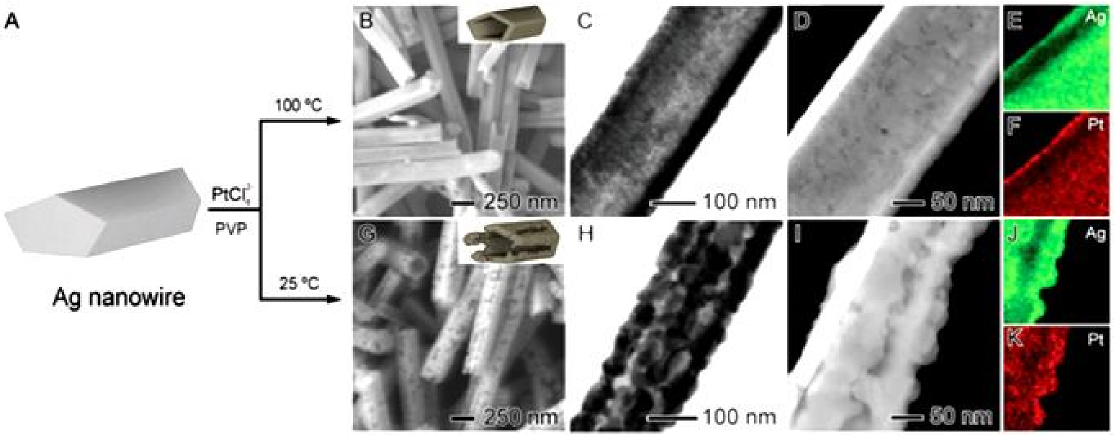


Fig. 8. (A) Galvanic replacement between Ag nanowires and $PtCl_6^{2-}$ ions performed either at 100 °C or room temperature, leading to the formation of smooth (B − F) or rough (G − K) surfaces, respectively, as shown in the SEM (B, G), HRTEM (C, H), STEM HAADF (D, I), and STEM EDX (E, F, J, K) images [34]

Conclusions

In modern nanotechnologies, galvanic replacement is a technologically effective method for synthesizing bimetallic Au/Ag, Pd/Ag, and Pt/Ag nanostructures on a sacrificial silver nanotemplate in aqueous solutions. Nanoscale galvanic replacement provides the controlled formation of hollow or porous nanostructures with ultrathin walls. The geometry and composition of these metallic nanostructures depend on the main factors of galvanic replacement, namely the nature of the deposited metal (Au, Pd, Pt), the solution composition, the ratio between the silver nanotemplate and the metal precursor, the duration and temperature of the replacement process. Only a complex approach to their influencing factors can provide the controlled synthesis of Au/Ag, Pd/Ag, and Pt/Ag nanostructures with predetermined characteristics. The shape of nanostructures synthesized by galvanic replacement mostly corresponds to the shape of the initial sacrificial template. The use of Au(I) precursor, compared to Au(III), provides a more controlled galvanic replacement. By adjusting the pH, the driving force of galvanic replacement and, accordingly, the morphology of the formed nanostructures can be regulated.

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СИНТЕЗ НАНОСТРУКТУР БІМЕТАЛІВ НА ЖЕРТОВНІЙ СРІБНІЙ НАНОМАТРИЦІ ГАЛЬВАНІЧНИМ ЗАМІЩЕННЯМ. ОГЛЯД

Висвітлено сучасний стан досліджень формування наноструктур біметалів гальванічним заміщенням. Показано ефективність гальванічного заміщення для контрольованого синтезу Au/Ag, Pd/Ag, Pt/Ag на жертовній срібній наноматриці у водних розчинах. Розглянуто особливості морфологічних та структурних змін жертовного наносрібла на різних стадіях заміщення. Проаналізовано залежності геометрії та складу наноструктур Au/Ag, Pd/Ag, Pt/Ag від головних параметрів гальванічного заміщення – природи та концентрації йонів відновлюваного металу, співвідношення між срібною наноматрицею і прекурсором металу, тривалості процесу, температури. Зроблено акценти на комплексний підхід до їх впливу для керованого одержання наноструктур Au/Ag, Pd/Ag, Pt/Ag із заданими характеристиками.

Ключові слова: срібна наноматриця, гальванічне заміщення, металеві наночастинки, наноструктури біметалів, порожнинні наночастинки.