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ТЕХНОЛОГІЯ НЕОРГАНІЧНИХ РЕЧОВИН ТА СИЛІКАТНИХ МАТЕРІАЛІВ

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INFLUENCE OF ULTRASOUND ON THE SYNTHESIS OF SILVER NANOPARTICLES BY GALVANIC REPLACEMENT IN SODIUM POLYACRYLATE SOLUTIONS

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Sonogalvanic replacement and galvanic replacement synthesis of silver nanoparticles (AgNPs) by magnesium scrap in sodium polyacrylate solutions were studied. It was found that during these processes in NaPA solutions silver is practically not deposited on the magnesium surface. Sodium polyacrylate provides stabilization of AgNPs with the formation of yellow solutions with maximum absorption of ~415 nm. It is shown that sonogalvanic replacement synthesis of AgNPs occurs due to the simultaneous course of galvanic replacement by magnesium and sonoreduction of Ag (I) by radicals and reducing agents. The rate of sonogalvanic replacement synthesis of AgNPs is 20-30% higher compared to galvanic substitution by mechanical stirring.

Key words: sonogalvanic replacement, silver nanoparticles, ultrasound, magnesium, sodium polyacrylate.

Introduction

In the last decade, much of the research has focused on the study of galvanic replacement (GR) as a universal method of obtaining functionally structured nanomaterials with controlled morphology for catalysis, plasmonics, sensory and biotechnology [1–3]. Galvanic replacement is a simple and effective method of modification of metal [4–6] and semiconductor [7–9] surfaces by metal nanostructures. A relatively new direction is GR synthesis of nanoparticles of mono- and bimetals [10–12].

Galvanic replacement – a spontaneous redox process between metal ions renewable M_1 and M_2 metal, which serves as a sacrificial template or substrate surface. According to the electrochemical mechanism, there is an electro generating half-reaction of oxidation of the sacrificial metal M_2 on the micro anode (1), which leads to a half-reaction of reduction of the metal M_1 on micro cathodes (2).

$$nM_2 \rightarrow nM_2^{m+} + me \quad (1)$$

$$mM_1^{n+} + ne \rightarrow mM_1 \quad (2)$$

In general, galvanic replacement is characterized by a total reaction (3).

$$mM_1^{n+} + nM_2 \leftrightarrow mM_1 + nM_2^{m+} \quad (3)$$

The course of galvanic replacement (3) is possible provided that the equilibrium potential $E_{M_2^{m+}/M_2}$ of the reducing metal is more negative than the equilibrium potential $E_{M_1^{n+}/M_1}$ of the reduced metal. By selecting metal templates, solutions of salts of renewable metals and process conditions, it is possible to synthesize nanostructures of precious metals in a controlled manner in terms of shape and size. In particular, the use of solutions containing surfactants, galvanic replacement produces stabilized metal nanoparticles in the volume of the solution [2].

The use of ultrasound is known in many chemical processes [13–15]. Ultrasound is also effective in the synthesis of metal nanoparticles by galvanic replacement [16–26]. This is primarily due

to the increase in the rate of the anode reaction (1), which is caused by the active renewal of the anode areas. As a result, the acceleration of the reduction reaction (2), which promotes the nucleation and formation of metal nanoparticles (MNPs).

The method of galvanic replacement using ultrasound as a controlled synthesis of mono- [16-19] and bimetallic [20-26] nanomaterials is the most studied for systems AgNPs [16, 19], AuNPs [17, 18], PtNPs [18], RuNPs [19], CuAgNPs [20, 21], Pd@CuNWs [22], Pd-AgNPs [23], Ni@PtNPs [24], PtCuNPs [25], Pd@Pt/CNPs [26]. Both nanoparticles and compact metals can serve as a sacrificial template for the synthesis of metal nanostructures. In particular, these are the active metals magnesium, aluminum [19], as well as iron [18] nickel [24], copper [16, 18, 20–22, 25], silver [17, 23], palladium [26].

One of the current areas of nanochemistry is the synthesis of solutions of silver nanoparticles which, due to their biological activity, exhibit antibacterial and antifungal properties [27]. Given the increased interest in this area of research, the aim is to establish the pattern of synthesis of stabilized AgNPs in sodium polyacrylate solutions under the combined action of ultrasound and galvanic replacement with magnesium scrap.

Materials and methods of research

For the synthesis of AgNPs nanoparticles by galvanic replacement used: of metal salt precursor argentum nitrate $AgNO_3$ (qualification "pure"), sodium polyacrylate (NaPA) (M = 2000) (qualification "chemically pure") – as a stabilizer, magnesium scrap (qualification "pure") fractional composition 0,75–1,0 mm as a reducing agent of Argentum ions.

The research was carried out in the following directions: synthesis of solutions of silver nanoparticles stabilized with sodium polyacrylate by galvanic replacemen under mechanical stirring and in the field of ultrasound; study of their main characteristics – absorption spectra and nanoparticle sizes.

Synthesis of AgNP performed in a solution of sodium polyacrylate and $AgNO_3$, which was placed in a glass thermostatted connected to an ultratermostat MLW UH8. The study was performed using an ultrasonic emitter magnetostrictive type Bandelin Sonopuls HD 2200.2 (Germany) at a power of 20 W, a frequency of 20 kHz. The working element of the ULTRASONIC emitter is a titanium horn (diameter – 12 mm). To 50 ml of NaPA solution was added magnesium scrap, turned on the ultrasound emitter, while adding a solution of $AgNO_3$. Then, with a certain interval of time, samples of the solution were taken to study the UV spectra. After completion of the experiment, the magnesium scrap was separated from the AgNPs solution by decantation. The obtained samples were stored in hermetically sealed glass containers made of dark glass.

The study was performed at a concentration of $AgNO_3$ of 0,2 mM, 5 g/dm^3 of NaPA, 0,25 g of magnesium scrap, and a reaction solution temperature of 20°C.

The UV-vis spectra of the colloidal solutions containing silver particles were recorded by UV/Vis spectrophotometer UV-3100PC (Shanghai Mapada Instruments Co., Ltd., China) using 1 cm cuvette at wavelength range 190–1100 nm. The comparison solution is distilled water.

TEM images of the samples were recorded using a JEM-I230 (JEOL, Tokyo, Japan) with an acceleration voltage of 80 kV. The samples for TEM investigations were prepared by drying of 0,05 μL of silver sol on the carbon grid at room temperature. The diameters of obtained AgNPs were determined using TEM images by comparison of the sizes of individual particles with the scales presented on images.

Research results and their discussions

The synthesis of solutions of silver nanoparticles in solutions of sodium polyacrylate by galvanic replacement has the following features. Ag^+ ions with electro-donor polymer anions PA^- form complex ions $[Ag_mPA]^{(n-m)-}$. Due to the electrons generated as a result of a reaction (4), complex ions of Argentum are reduced with the formation of nanoclusters $[Ag(0)_mPA]^{n-}$ (5).

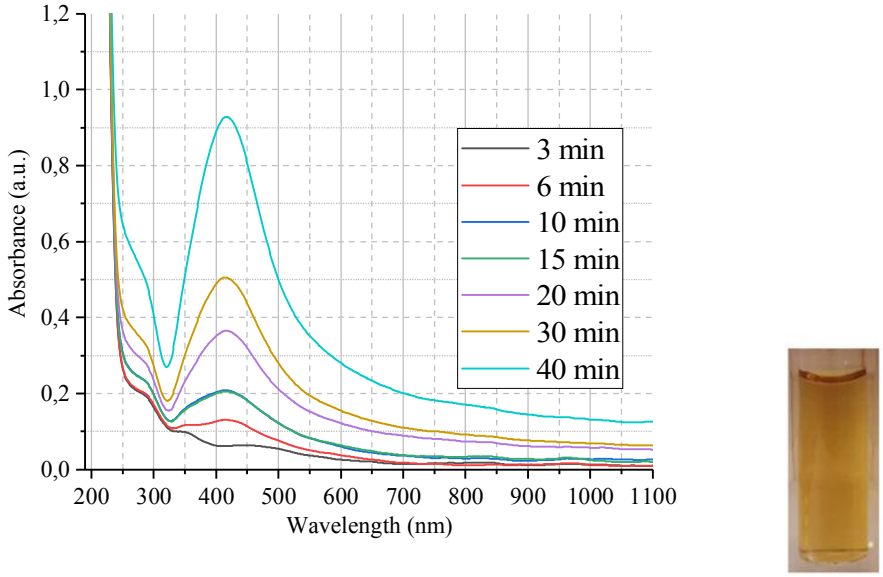
$$m/2Mg \rightarrow m/2Mg^{2+} + me. \quad (4)$$

$$[Ag_mPA]^{(n-m)-} + me \rightarrow [Ag(0)_mPA]^{n-}. \quad (5)$$

The formation of silver nanoparticles with magnesium can be described by the generalized equation of galvanic replacement (6).

$$[Ag_mPA]^{(n-m)-} + m/2Mg \rightarrow [Ag(0)_mPA]^{n-} + m/2Mg^{2+}. \quad (6)$$

The use of magnesium as an active sacrificial metal provides a large difference between the values of the standard electrode potentials of the half-reactions (4) and (5). This achieves a high rate of recovery and, accordingly, the nucleation of silver. Sodium polyacrylate stabilizes AgNPs with the formation of yellow solutions with an absorption maximum of ~ 415 nm (Fig. 1).



a *b*

Fig. 1. UV-Vis absorption spectrum (a) and images (b) of AgNPs in 5 g/dm^3 NaPA solution after galvanic replacement of 0,5 g magnesium scrap for 40 min, 0,2 mM $AgNO_3$, for 20 ^oC

During the whole process of galvanic replacement in NaPA solutions, silver is practically not deposited on the magnesium surface during intensive stirring. It provides renewal of the magnesium surface, which promotes a stable rate of reactions (4, 5) and, accordingly, the nucleation and formation of AgNPs. The latter is stabilized by the surfactant and passes from the surface of magnesium into the volume of the solution. Thus, mechanical and hydrodynamic effects and PA^- anions prevent the deposition of silver on the surface of the sacrificial metal.

In the ultrasonic field, as a result of sonogalvanic replacement, similar solutions of yellow silver nanoparticles with a slightly lower absorption maximum of ~410 nm are formed (Fig. 2, *a*). However, the rate of synthesis is 20–30% higher compared to galvanic replacement by mechanical mixing (Fig. 1). This is due to the action of ultrasound and related phenomena. Thus, in the field of action of ultrasound, acoustic microflows and acoustic cavitation are formed in the solution. Acoustic microflows significantly increase the mass transfer at the metal-liquid interface by reducing the ion concentration gradient. High temperature and pressure inside cavitation bubbles initiate the formation of free radicals (H·; ·OH, R·) and products of their interaction (H_2O_2, O_2) [14], which cause sonoreduction (7–9). The collapse of cavitation bubbles leads to the formation of intense microcurrents of fluid and shock waves. Thus, sonogalvanic replacement synthesis of AgNPs occurs due to the simultaneous course of two main processes: 1) galvanic replacement with magnesium and 2) sonoreduction of Ag (I) by radicals and reducing agents.

$$[Ag_mPA]^{(n-m)-} + H\cdot \rightarrow [Ag(0)_mPA]^{n-}. \quad (7)$$

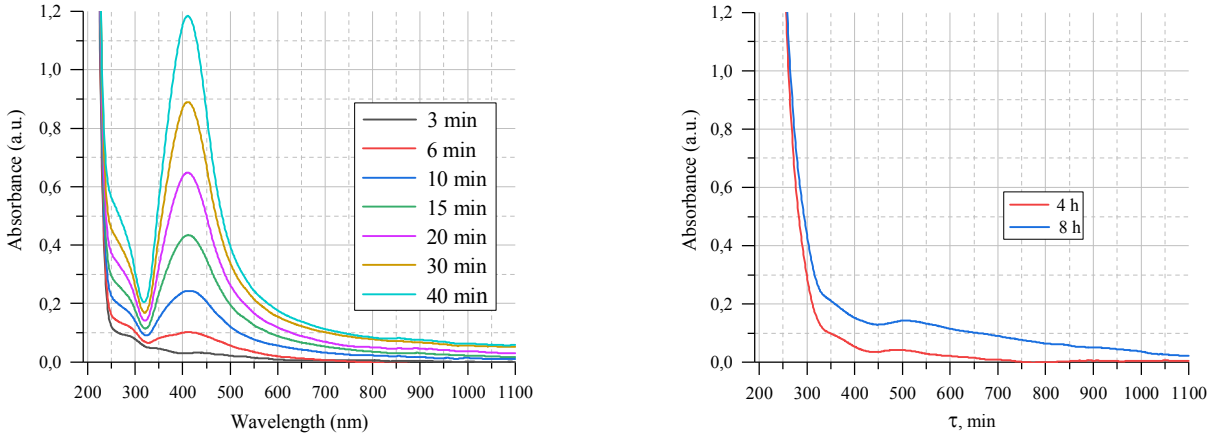
$$[Ag_mPA]^{(n-m)-} + R\cdot \rightarrow [Ag(0)_mPA]^{n-}. \quad (8)$$

$$[Ag_mPA]^{(n-m)-} + H_2O_2 \rightarrow [Ag(0)_mPA]^{n-}. \quad (9)$$

To study the effect of sonoreduction, a control experiment was performed in the absence of magnesium scrap. No discoloration of the solution was observed during 4 hours of ultrasound examination. Weak and broad absorption spectra with a maximum of about 520 nm after 8 hours of ultrasonic treatment (Fig. 2, *b*) indicate a low content of nanoparticles and a wide size distribution due to the small number of free radicals formed. This confirms that in sonogalvanic replacement synthesis

of AgNPs the predominant share belongs to galvanic replacement magnesium.

The dependences of the absorption intensity of AgNPs on the duration of the experiment are linear, which indicates the stability of both sonogalvanic replacement and galvanic replacement processes (Fig. 3). The rate of sonogalvanic replacement synthesis of AgNPs is 20–30 % higher compared to galvanic substitution by mechanical stirring.



a *b*

Fig. 2. UV-Vis absorption spectrum of AgNPs in 5 g/dm^3 NaPA solution, 0,2 mM $AgNO_3$, after sonogalvanic replacement of 0,5 g magnesium scrap(a) and in the absence of magnesium scrap (b)

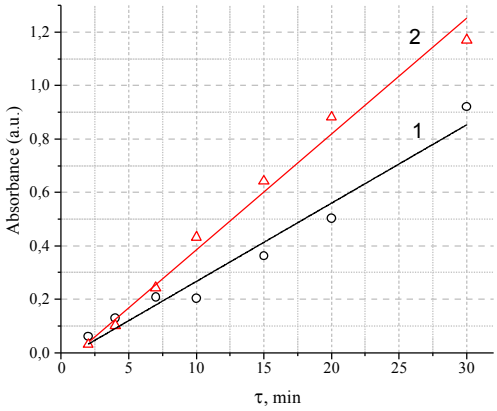
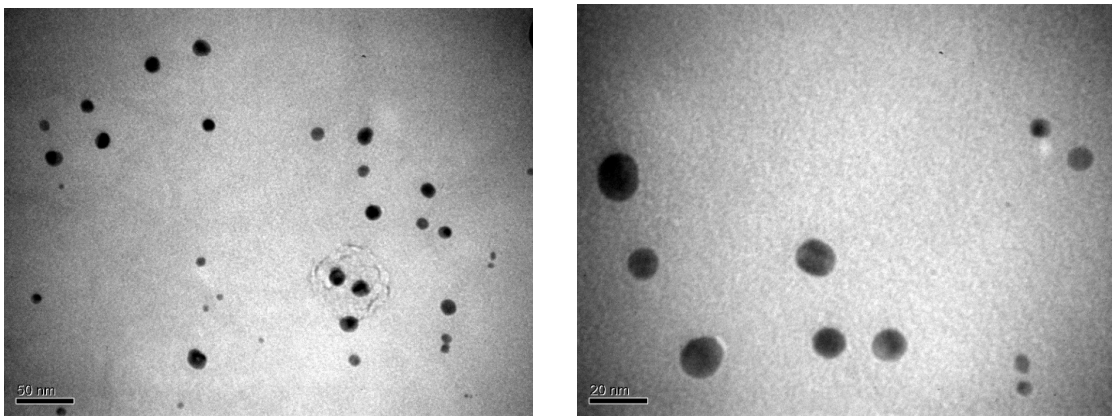


Fig. 3. Dependencies of the change of optical density of solutions AgNPs on time during galvanic replacement (1) and sonogalvanic replacement (2) at $CAgNO_3$ = 0,2 mM, mMg = 0,25g, 20 °C

Sonogalvanic replacement synthesis of AgNPs provides the formation of spherical nanoparticles with a size of not more than 15 nm with a small scatter in diameter (Fig. 4).

Conclusions

During sonogalvanic replacement and galvanic replacement in NaPA solutions, silver is practically not deposited on the magnesium surface. Sonogalvanic replacement synthesis of AgNPs occurs due to the simultaneous course of galvanic replacement by magnesium and sonoreduction of Ag (I) by radicals and reducing agents. The predominant share belongs to galvanic replacement by magnesium. The rate of sonogalvanic replacement synthesis of AgNPs is 20–30 % higher compared to galvanic substitution by mechanical stirring. The linear nature of the dependence of the absorption intensity of AgNPs on the duration of the experiment indicates the stability of both sonogalvanic replacement and galvanic replacement processes.



a *b*

Fig. 4. TEM images at different magnifications (a, b) of AgNPs, synthesized in NaPA solution (g/dm^3), 0,2 mM $AgNO_3$ after sonogalvanic replacement of magnesium for 40 min

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ВПЛИВ УЛЬТРАЗВУКУ НА СИНТЕЗ НАНОЧАСТИНОК СРІБЛА ГАЛЬВАНІЧНИМ ЗАМІЩЕННЯМ У РОЗЧИНАХ НАТРІЮ ПОЛІАКРИЛАТУ

Досліджено синтез наночастинок срібла (AgNPs) магнієвим скрапом у розчинах натрію поліакрилату соногальванічним та гальванічним заміщенням. Встановлено, що впродовж цих процесів у розчинах NaPA срібло практично не осідає на магнієвій поверхні. Натрію поліакрилат забезпечує стабілізацію AgNPs з утворенням розчинів жовтого забарвлення з максимумом поглинання ~415 нм. Показано, що синтез AgNPs соногальванічним заміщенням відбувається внаслідок одночасного перебігу гальванічного заміщення магнієм і відновлення Ag(I) за допомогою радикалів і відновників. Швидкість синтезу AgNPs соногальванічним заміщенням є на 20–30 % більшою порівняно з гальванічним заміщенням за механічного перемішування.

Ключові слова: соногальванічне заміщення, наночастинки срібла, ультразвук, магній, натрію поліакрилат.